

Article

The Reasons for Different Kinetics of the Norrish-Yang Reaction in Crystals. Structural and Spectroscopic Studies

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by the Johnson-Mehl-Avrami-Kolmogorov model. In the first stage the reaction progresses homogeneously at a constant rate, but for the second mode, which started at ca. 50% conversion, the reaction progresses with autoinhibition. The reasons for this autoinhibition are (i) the changes in the geometry of the reaction center during the second stage, which were not observed in the first stage, (ii) the C–H··· π interactions, which become stronger along with the reaction progress, and (iii) the change in character of the carboxylate group toward the carboxylic-like group. The Norrish-Yang reaction also proceeds in crystals at 0.2 GPa, as stated on the grounds of the characteristic changes in the unit cell parameters along with UV irradiation.

INTRODUCTION

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During the Norrish-Yang reaction an achiral reactant molecule transforms into a chiral photoproduct molecule. The accomplishing of reactions in an enantioselective way is one of the challenges in organic chemistry. Since the Norrish-Yang reaction in a crystalline state can be conducted in a more controlled manner than in solution, it attracts the interest of many organic chemists.¹⁻⁸ Its advantage over reactions conducted in solutions is mainly connected with the possibility to correlate chemical behavior (kinetics, stereochemistry) with a crystal structure. It is worth adding that the reaction in a crystalline state can proceed differently than in solutions owing to different geometrical parameters for both media. The Norrish-Yang reaction is a photochemical process that takes place in compounds having a carbonyl group and a γ -hydrogen atom and that leads to a four-membered ring through a 1,4biradical (Scheme 1, path 1). The formation of the 1,4biradical is named the Norrish type II reaction, and the recombination leading to the ring is known as the Yang cyclization.⁹ In special cases, when except for γ -hydrogen there is δ -hydrogen in a molecule, it is possible that a 1,5-biradical and afterward a five-membered ring is formed (Scheme 1, path 2). There are known cases when only one type of ring or simultaneously both types of them are obtained in one crystal.7,10

reaction in the studied compound proceeds in two stages described

The fact as to whether the ring is formed, and which of the two above-mentioned rings (four-membered or five-membered) occurs, depends on several factors. Among the most crucial, the geometry of the reaction center must be Scheme 1. Norrish-Yang Reaction (Path 1) and the Yang Cyclization to a Five-Membered Ring (Path 2)



considered. This geometry can be described by five parameters: d, D, Δ , θ , and ω .^{11,12} Below they are presented for the case of the Norrish-Yang reaction (Scheme 2):

- *d*—the distance between the γ -hydrogen and carbonyl oxygen atoms; the ideal value is less than 2.7 Å.¹¹
- *D*—the distance between two carbon atoms forming the new covalent bond; the ideal value is less than 3.2 Å.¹²

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Scheme 2. Graphical Representation of the Geometrical Parameters Describing Susceptibility to the Norrish-Yang Reaction



- Δ —the C=O···H angle between the atoms of the carbonyl group and γ -hydrogen; the ideal value is 90°-120°.¹¹
- θ —the C-H···O angle between γ -carbon, γ -hydrogen, and carbonyl oxygen; the ideal value is 180° .¹³
- ω—the torsion angle describing the deviation of the γhydrogen from the plane of the carbonyl group; the ideal value is 0°.¹⁴

The above-given ideal values are also valid in the case of the formation of a five-membered ring, except for the value of parameter D, which in such a situation should be less than 3.4 Å.¹⁵

At times, the analysis of parameter d only enabled the rationalization of photochemical reactivity in crystals, as it was in the case of the Yang cyclization of α -1-norbornylacetophenone derivatives.^{2,8} The analysis of d and Δ explained the predominant formation of a five-membered ring (not fourmembered) for phenylethaneaminium 4-(2,4,6-triisopropylbenzoyl)benzoate.⁷

Nevertheless, there were also cases when the analysis of all five parameters provided valuable results, for instance, when explaining why only one of two *o*-isopropyl groups was reactive^{6,16–18} and why there were differences in the reactivity of three salts of 4-(2,4,6-triisopropylbenzoyl)benzoic acid.¹⁸ However, there were cases where the analysis of the geometrical parameters merely explained the occurrence of the reaction but did not provide the answer as to why only one of the two fragments having a similar geometry took part in the reaction.¹⁹ In terms of the geometrical demands for benzophenones, the role of the dihedral angle between a carbonyl group and a benzene ring was also emphasized.²⁰

According to the topochemical postulate, a photochemical reaction proceeds in crystals when there is the possibility of breaking old bonds and forming new ones. Such a reaction is easier when the required atomic shifts are small and a reaction cavity^{21–27} does not significantly change its geometry.^{28,29} However, when there is free space close to the reacting molecular fragments, the reaction can occur, although the necessary shifts and changes are significant. Moreover, the existence of such a free space can cause a crystal lattice to better accommodate a strain caused by the appearance of product molecules. The analysis of the size and shape of a reaction cavity of suitable shape facilitated a photochemical reactivity of many compounds.^{22,24–27,30–32} It was reported that a big reaction ^{33–35} and a small cavity of unsuitable shape disabled a reaction.²⁰ The geometry of a reaction cavity was responsible for the reaction rate, ^{36–40} the reaction direction, and the obtained products.^{5,19,41} Not only was the geometry of a

reaction cavity analyzed but also elasticity compensating strains caused by a reaction and protecting crystals from cracking.^{42–46} The feedback was the factor responsible for kinetics in the case of various compounds.^{43,44,47–50} Sometimes the analysis of one or several individual intermolecular contacts provided valuable information connected to the proceeding photochemical reactions in crystals. For instance, hydrogen bonds were given as the reason for photochemical inertia^{\$1-53} or activity.^{18,54} $\pi \cdots \pi$ interactions had a positive influence on reactivity by preorientating molecules in crystals.^{55,56} or a negative impact by impeding atomic shifts.^{20,57}

The above-described factors are connected with internal crystal structures. It should be added that, except for these, there are other factors, which are external, such as radiation wavelength, temperature, and pressure.⁵⁹

The kinetics of a photochemical reaction in a crystal can be described in terms of the Johnson-Mehl-Avrami-Kolgomorov (JMAK) model by the following equation:^{58,60}

$P = 1 - \exp(-kt)^n$
where:
P is product content.
c is reaction rate.
is time.
<i>i</i> is the Avrami exponent.

The *n* parameter provides the information about dimensionality of product growth *D*. For *n* equal to 2, 3, or 4 the formation of product proceeds in 1, 2, or 3 dimensions, respectively. In the case when *n* is 1, there are no vectors of product propagation, and product molecules occur independently and randomly. In such a situation, domains that could cause undesirable phase separation are not formed, and a reaction is homogeneous. It should be mentioned that certain circumstances arose in which the values of the Avrami exponent were significantly different from integers.^{61,62} In practice the logarithmic form of the JMAK equation, known as the Avrami plot, is used. The linear dependence between ln[-ln(1 - P)] and ln t justifies the use of the model.

The JMAK model was applied to photochemical reactions such as the [2 + 2] photodimerization of α -trans-cinnamic, ^{61,63} β -cinnamic, ⁶⁴ o-methoxycinnamic, and o-ethoxycinnamic acids⁶⁵ and the [4 + 4] photodimarization of 9-anthracenecarboxylic acid.⁶⁶ It was also used for the description of the kinetics of the Norrish-Yang reaction in crystals of ammonium and benzylaminium 4-(2,4,6-triisopropylbenzoyl)benzoates. The analyses performed revealed a homogeneous mechanism with autoinhibition for the ammonia salt, n = 0.84, and a hybrid mechanism (homogeneous and one-directional) for the benzylamine salt, n = 1.44(4).¹⁸ A very interesting phenomenon was met in the case of the benzylidene oxazolone derivative, where the kinetics significantly changed at a certain stage of the process, as it was evidenced by two straight lines having different slopes in the Avrami plot. During the first stage, the reaction was homogeneous, n = 1.1(2), and during the second one it proceeded homogeneously with autoinhibition, n = 0.33(6). The observed autoinhibition was connected with certain, yet gradual, degradation of a crystal.⁶⁷ In this paper, we aim to reveal and explain on structural grounds the differences in the unique kinetics of the Norrish-Yang reaction in crystals in the case of 1,3,5,7-tetraazatricyclo-[3.3.1.13,7]decane 4-(2,4,6-triisopropylbenzoyl)benzoate by means of X-ray diffraction and additionally by Raman spectroscopy.

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Fable 1. Experimenta	l Data for	the Selected	Structures
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pressure	0.1 MPa	0.1 MPa	0.1 MPa	0.2 GPa
product content/%	0	48.1(8)	100	0
chemical formula	$C_{29}H_{40}N_4O_3$	$C_{29}H_{40}N_4O_3$	$C_{29}H_{40}N_4O_3$	$C_{29}H_{40}N_4O_3$
formula weight, g/mol	492.65	492.65	492.65	492.65
crystal system, space group	monoclinic, $P2_1/c$	monoclinic, $P2_1/c$	monoclinic, $P2_1/c$	monoclinic, $P2_1/c$
a, b, c, Å	26.6710(13), 8.6190(5), 11.8835(6)	26.308(2), 8.7899(7), 11.9218(8)	25.8752(12), 9.0770(4), 11.8468(5)	26.50(2), 8.5258(8), 11.7775(11)
β , deg	92.660(5)	93.491(6)	94.268(4)	92.72(2)
<i>V</i> , Å ³	2728.8(2)	2751.7(4)	2774.7(2)	2658(2)
Ζ	4	4	4	4
D_{x} Mg/m ³	1.199	1.189	1.179	1.231
μ , mm ⁻¹	0.078	0.078	0.077	0.080
crystal size, mm	$0.60 \times 0.40 \times 0.03$	$0.60 \times 0.40 \times 0.03$	$0.60 \times 0.40 \times 0.03$	$0.40 \times 0.36 \times 0.04$
temperature, K	295(2)	295(2)	295(2)	295(2)
completeness, %	100	100	100	31.3
No. of reflections	10 655	18 479	18 056	13 325
No. of independent reflections	5640	5417	5460	1504
No. of observed reflections	3699	3105	2374	717
R _{int}	0.026	0.040	0.065	0.194
$R_1 \left[F^2 > 2\sigma(F^2) \right]$	0.058	0.053	0.064	0.085
$wR_2 \left[F^2 > 2\sigma(F^2)\right]$	0.117	0.117	0.136	0.203
S	1.029	1.030	1.000	1.020
$\rho_{\rm max}$ $\rho_{\rm min}$ e Å ⁻³	0.16, -0.19	0.16, -0.15	0.21, -0.16	0.17, -0.15

EXPERIMENTAL SECTION

4-(2,4,6-Triisopropylbenzoyl)benzoic acid was prepared by the acylation of 1,3,5-triisopropylbenzene with 4-carbomethoxybenzoyl chloride followed by the basic hydrolysis of the obtained product, according to the procedure in the literature.⁶⁸ To form the salt, the stoichiometric amount of 1,3,5,7-tetraazatricyclo[3.3.1.13,7]decane (urotropine) was added to 4-(2,4,6-triisopropylbenzoyl)benzoic acid dissolved in ethanol. The crystals suitable for X-ray diffraction experiments were obtained after recrystallization from a mixture of ethanol and toluene (v/v 5:1).

Two crystals at ambient pressure (crystals 1 and 2) and one crystal at 0.2 GPa (crystal 3) were examined. Crystal 2 was studied to compare the kinetics of the Norrish-Yang reaction with that in crystal 1. The high-pressure data were collected using a Boehler-Almax diamond anvil cell (DAC).⁶⁹ Quartz was used as a high-pressure sensor according to the method developed by Angel et al.,70 and glycerine was used as a hydrostatic pressure medium. The photochemical reaction was induced by means of a 100 W Hg lamp equipped with a water filter and a BG-39 glass filter. Crystal 1 was irradiated for 5, 10, 20, 40, 60, 90, 160, 280, and 460 min, crystal 2 for 20, 40, and 80 min, and crystal 3 for 5, 10, and 20 min in total. Before the irradiation, and after each of them, X-ray data were collected. The crystal structures were determined by means of SHELXS, SHELXT, and SHELXL⁷¹⁻⁷³ implemented in Olex2⁷⁴ for crystals 1 and 2 for all irradiation times except crystal 1 after 60 min of irradiation and for crystal 3 before irradiation.

For pure reactant crystals 1 and 2, all non-hydrogen atoms were refined anisotropically. For the structures containing both the reactant and the product, the atoms in the carbonyl, hydroxyl, and reactive *o*-isopropyl groups and in ring C8 \rightarrow C13 were refined independently for the reactant and the product, but the positions of the remaining atoms were kept the same for both components. The atoms of the major component were refined anisotropically, and isotropically they were refined for the minor one. In all structures the hydrogen atoms were positioned geometrically and treated as riding, except the hydroxyl hydrogen, which was omitted in the partly reacted crystals and the hydrogen at N1 forming the hydrogen bond with the 4-(2,4,6-triisopropylbenzoyl)benzoate anion, which was refined freely in the case of crystal 1. For the disordered structures DFIX, DANG, SIMU, and occasionally FLAT restraints were used. The product content was

determined on the grounds of the site occupation factor. The selected experimental data are gathered in Table 1, and the full data for all structures are given in the cif files (see the Supporting Information).

The Raman spectra for crystal 1 before and after different periods of UV exposure were recorded using a dispersive spectrometer (LabRAMHR800 Horiba Jobin Yvon) equipped with a He–Ne laser operated at 633 nm. The measurements were conducted for a 4000–100 cm⁻¹ range and spectral resolution of 2.5 cm⁻¹. For a comparison of the spectra, the intensities of the bands were normalized in relation to the band at 1600 cm⁻¹ resulting from a CC aromatic ring stretching mode.

RESULTS AND DISCUSSION

1,3,5,7-Tetraazatricyclo[3.3.1.13,7]decane 4-(2,4,6triisopropylbenzoyl)benzoate undergoes the Norrish-Yang reaction in a crystalline state. Of two potentially reactive oisopropyl groups, 2-isopropyl only takes part in the formation of the product, which is presented in Figure 1a-c. As can be seen in this figure, the product molecule does not significantly change its position with respect to the reactant molecule. The shifts of atoms are only observed for the reactive 2-isopropyl group, carbonyl group, and aromatic ring $C8 \rightarrow C13$. There are two main kinds of factors supporting the reactivity of 2isopropyl: (i) the values of the geometrical intramolecular parameters in the region of this group, suitable for the Norrish-Yang reaction, and (ii) the volume of the void adjacent to it, allowing shifts of atoms during the reaction. The values of the intramolecular geometrical parameters for both o-isopropyl groups, together with the ideal and literature ranges, are presented in Table 2, and the voids can be seen in Figure 1d,e. Evidently, for 2-isopropyl the values of these parameters are closer to the ideal ones, and the void is relatively large. The geometry for 6-isopropyl is less favorable for the Norrish-Yang reaction, and there is no free space of a suitable size and shape near this group.

The relationship between the product content and the irradiation time is shown in Figure 2a,b for crystals 1 and 2. Since we determined the crystal structures for many stages of



Figure 1. ORTEP⁷⁵ view of (a) the reactant molecule in the pure reactant crystal, (b) the reactant and product molecules for 48.1% reaction progress, and (c) the product molecule in the pure product crystal together with the atom labels. The atomic displacement ellipsoids were drawn at a 20% probability level. The free space around the reactant molecule at (d) ambient pressure and (e) 0.2 GPa (the void near 2-isopropyl shown by the arrow). The radius of the ball localizing the free space was 0.9 Å, and the grid spacing was 0.2 Å.⁷⁶

Γable 2. Geometrical Reactiv	v Parameters for <i>o</i> -Isopropyl	Groups of the Studied Compound
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				_	_		
		d [Å]	D [Å]	$\omega [deg]$	Δ [deg]	$\theta \; [deg]$	free space ^{<i>a</i>} $[Å^3]$
0.1 MPa	2-isopropyl	2.67	2.934(3)	75.5	64.8	122.9	16.0(4)
	6-isopropyl	3.10	2.955(3)	87.0	48.1	114.7	0
0.2 GPa	2-isopropyl	2.7	2.99(2)	73	67	123	14.0(3)
	6-isopropyl	3.1	2.91(1)	88	46	115	0
ideal		<2.7	<3.2	0	90-120	180	
literature range ^b		2.39-3.15	2.82-3.12	50.8-86.0	46.8-88.0	104.3-145.0	

^{*a*}The radius of the ball localizing the free space was 0.9 Å, and the grid spacing was 0.2 Å.^{76 b}On the basis of the search in Cambridge Structural Database, ver. 1.19.⁷⁷

the reaction, including the structures before the reaction and after 100% conversion, we were able to study the reaction kinetics in detail by means of the Johnson-Mehl-Avrami-Kolgomorov model (see Introduction). As shown in Figure 2c,d, we can distinguish two lines having different slopes in the Avrami plots. This means that the reaction kinetics is different for the first and second stages of the crystal photochemical transformation. For the first stage the Avrami exponent n is ~1 (0.93 and 1.08 for crystals 1 and 2, respectively), which indicates that the mechanism of the reaction is homogeneous

and also that the occurring structural transformations brought about by the reaction do not influence further product formation. In the second stage, n is much less than 1 (0.44 and 0.52 for crystals 1 and 2, respectively), which indicates that the reaction proceeds with autoinhibition; that is, the further product formation makes the reaction more difficult. It is worth pointing out that, for both studied crystals, the values of n are approximately the same.

The observed autoinhibition means that the more product molecules that exist (and the fewer the reactant molecules),



Figure 2. Relationship between the product content and UV irradiation time for (a) crystal 1 and (b) crystal 2. The Avrami plot for the Norrish-Yang reaction in (c) crystal 1 and (d) crystal 2. (\blacksquare) First and (\bullet) second stages of the reaction.

the more difficult the reaction is. In connection with this statement, we analyzed the environment of reactant molecules after 20 min of UV irradiation (i.e., for the first stage of the reaction) and after 160 min (i.e., for the second stage) for four border situations:

- The crystal is in the first stage of the reaction, and one reactant molecule is only surrounded by other reactant molecules.
- (2) The crystal is in the first stage of the reaction, and one reactant molecule is only surrounded by product molecules.
- (3) The crystal is in the second stage of the reaction, and one reactant molecule is only surrounded by other reactant molecules.
- (4) The crystal is in the second stage of the reaction, and one reactant molecule is only surrounded by product molecules.

This analysis revealed that, near the reactive 2-isopropyl group, there is a free space of a similar size and shape for all four cases, that is, for both stages of the reaction and regardless of the vicinity of the reactant molecule. This observation indicates that the autoinhibition is not the result of free space reduction with the reaction progress. The free space for the first situation above is shown in Figure 1d.

To find the reason for the reaction autoinhibition, we analyzed the geometry of the reaction center and state that this geometry was one of the main reasons for the photochemical behavior of the crystals during the first and the second stages of the reaction. The likelihood of the Norrish-Yang reaction can be predicted on the grounds of five intramolecular geometrical parameters: d, D, ω , Δ , and θ (see the

Introduction). It should be emphasized here that, because of the geometry of the reaction center, the formation of a fivemembered ring was not possible: the value of parameter d was greater than 3.3 Å, and that of parameter D was greater than 3.8 Å.

As written above, at the beginning of the photochemical crystal transformation, the geometrical parameters have values favorable for the Norrish-Yang reaction with the participation of 2-isopropyl. Along with the reaction progress the values of parameters d, Δ , and ω become less favorable for 2-isopropyl and more favorable for 6-isopropyl, which can be concluded from Figure 3, which shows that parameter D decreases for 2isopropyl and 6-isopropyl and that the remaining parameter θ is constant for both groups. It is interesting that in the first stage of the reaction, that is, until ca. 50% conversion, the values of the parameters do not change significantly; only in the second stage this is the case. The changes in the values of *d*, Δ , and ω explain the change in the kinetics, namely, near the 50% reaction progress stage, the geometry of the reaction center starts to worsen for 2-isopropyl and improve for 6isopropyl. Nevertheless, 6-isopropyl does not participate in the reaction (see above for the insufficient free space).

The additional reason for the observed autoinhibition connected with intramolecular geometry is the change in the orientation of aromatic ring $C1\rightarrow C6$ in relation to the carbonyl group: the value of the dihedral angle between $C1\rightarrow C6$ and the plane formed by atoms C1, C7, O1, and C8 gets worse from 79.1° to 86.5°.

Intermolecular interactions can also influence the autoinhibition of the reaction. The important contacts in this context seem to be $C-H\cdots\pi$ interactions presented in Figure 4. Although such contacts are obviously not as strong as typical



Figure 3. Change in values of the geometrical intramolecular parameters describing the susceptibility to the Norrish-Yang reaction for 2-isopropyl (\blacksquare) and 6-isopropyl (red \bullet).

hydrogen bonds, they can act cooperatively.^{78,79} Along with the reaction progress, the mean distance for them becomes shorter, which can make the shift of ring C8 \rightarrow C13 necessary for making the four-membered ring formation more difficult.

The next explanation of the autoinhibition of the studied reaction was provided by the Raman spectra shown in Figure 5. The bands characteristic for the C=O stretching mode in ketones at 1680 cm⁻¹ and for the phenyl-carbon stretching in aryl ketones at 1255 cm⁻¹ decline along with the photochemical reaction progress and finally disappear, which is connected with the formation of the hydroxyl group from the carbonyl group. These spectral features are accompanied by the increase in the intensity of the band characteristic for the C-O stretching vibrations in alcohols at 1030 cm⁻¹ and the appearance of the bands characteristic for the O-H stretching at 3576 and 3612 cm⁻¹. In terms of the autoinhibition it is important that, along with the reaction progress, the characters of the N-H…O hydrogen bond and of the carboxylate group strongly change. It results from the determined X-ray structures indicate that the N…O distance decreases monotonically, which is presented in Figure 6. The observed reduction is conjugated with the changes in the position of the hydrogen atom in this bond. At the beginning of the reaction, the hydrogen atom is situated at nitrogen at a distance of 1.04 Å, which indicates the salt formation. Afterward along with the reaction progress it moves away from nitrogen toward oxygen, and at the end of the reaction it is found almost in the middle between both these atoms. The changes in the position of the hydrogen atom influence the changes in the electronic structure of the carboxylate group, which is also shown in Figure 6.



Figure 4. Changes in the C-H··· π contacts along with the Norrish-Yang reaction progress. The progress of the reaction is presented from red through pink to gray. D_{atm} is the distance between the hydrogen atom and the closest sp² atom, C9···H29aⁱ (\blacksquare), C11···H27aⁱ (\blacklozenge), C13···H28aⁱ (\blacktriangle). The symmetry code: i = x, 1/2 - y, -1/2 + z.

Before the photochemical reaction, this group is stabilized by a resonance effect, and the difference in CO bond lengths is only ca. 0.02 Å (1.264 vs 1.245 Å). This delocalization gradually decreases along with the reaction progress, and in the final step the difference in the CO bond lengths increases to 0.06 Å (1.286 vs 1.223 Å), and the geometry of the carboxylate group is closer to that of a carboxylic. This is accompanied by changes in the Raman spectra: the band at 1646 cm⁻¹ characteristic for the stretching mode of the benzoic acid carbonyl⁸⁰ appears and gradually increases along with the reaction progress, and the strong symmetric carboxylate anion stretching at 1387 cm⁻¹ decreases, both evidencing that the electron charge in the carboxylate becomes less delocalized.

This carboxylic-like structure is revealed in the Raman spectra after ca. 50% reaction progress, that is, at the stage when reaction kinetics changes, which suggests that the change in the reaction kinetics can be associated with the alterations in the character of the carboxylate group (electron donating) toward the carboxylic group (electron withdrawing). It is worth adding that the electron effects of the above-described type can be indicated as the next explanation of the



Figure 5. Raman spectra for crystal 1.

observation made in the past that 4-(2,4,6-triisopropylbenzoyl)benzoic acid undergoes the Norrish-Yang reaction in crystals with difficulty.²⁰

The structural transformations induced by the Norrish-Yang reaction also include modifications in the values of the unit cell parameters: parameter *a* decreases, and *b* increases, both in a monotonic manner; *c* remains almost constant, and the angle β becomes more obtuse along with the reaction progress, which is presented in Figure 7. The values of the cell parameters also change with the progress of the reaction conducted at 0.2 GPa. The character of these changes is the same as at ambient pressure: after 10 min of UV irradiation of the crystal, *a* decreases from 26.50(2) to 26.34(8) Å, *b* increases from 8.5258(8) to 8.601(3) Å, *c* almost does not alter (11.7775(11) vs 11.767(3) Å), and β increases from 92.72(2)° to 93.23(8)°. All these photoinduced modifications indicate that the Norrish-Yang reaction of the studied compound also proceeds at 0.2 GPa.

To gain knowledge about the influence of high pressure on the kinetics of the Norrish-Yang reaction of the studied compound, at first we analyzed the influence of high pressure on intra- and intermolecular geometry. It can be said that there are no changes in the intramolecular geometry with the increase of pressure, even in the geometry of the reaction center. Moreover, the high pressure of 0.2 GPa does not have a significant impact on intermolecular interactions in which the atoms of the reaction center take part. In accordance with this, the free space existing near the reactive 2-isopropyl group in ambient conditions is also observed at high pressure (see



Figure 6. Changes in the geometry of (a, b) the N···H···O hydrogen bond and (c) the carboxylate group along with the reaction progress.

Figure 1e), and its volume is 16.0(4) and 14.0(3) Å³, respectively. On the one hand, the above findings indicate that the kinetics of the Norrish-Yang reaction of the studied compound should be similar at ambient pressure and 0.2 GPa. On the other hand, it should be taken into account that, in ambient conditions, the studied photochemical reaction proceeds with the increase of the unit cell volume (see Figure 7) and that high pressure by counteracting this increase should decrease the reaction rate. The decrease of the rate of the Norrish-Yang reaction at high pressure was also observed in the case of another compound.⁸¹



Figure 7. Changes in the values of the cell parameters at ambient pressure.

CONCLUSIONS

The X-ray diffraction and Raman spectroscopy studies were undertaken in order to describe the kinetics of the Norrish-Yang reaction of 1,3,5,7-tetraazatricyclo[3.3.1.1^{3,7}]decane 4-(2,4,6-triisopropylbenzoyl)benzoate in crystals. The Norrish-Yang reaction proceeds with the participation of the 2isopropyl group. The overall shape and size of reactant and product molecules is very similar: only the reacting fragments and one aromatic ring shift significantly as a result of the reaction. The studies revealed that the reaction kinetics changes at ca. 50% conversion. The two stages of the reaction were described by the JMAK model. In the first stage the reaction proceeds homogeneously with a constant rate, but in the second stage it proceeds with autoinhibition. The observed autoinhibition is a result of the changes in the molecular geometry, in the crystal lattice structure, and in the electron properties of substituents. The Norrish-Yang reaction also proceeds in crystals at 0.2 GPa, which was stated on the grounds of the characteristic changes in the unit cell parameters along with the reaction progress. The reaction should proceed slightly slower at 0.2 GPa, because high pressure counteracts the unit cell increase, which is demanded for the reaction to proceed. The pressure of 0.2 GPa does not have influence on the intramolecular geometry and the volume of the free space near the reaction center.

ASSOCIATED CONTENT

Accession Codes

CCDC 1978380–1978398 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

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