

# Monitoring structural transformations in crystals. 13. On photocyclization in 2,3,4,5,6-pentamethylbenzophenone, 1,3-diphenylbutan-1-one and 2,4,6-triisopropyl-4'-methoxybenzophenone

Julia Bąkiewicz and Ilona Turowska-Tyrk\*

Faculty of Chemistry, Wrocław University of Technology, 27 Wybrzeże Wyspiańskiego, 50-370 Wrocław, Poland

Correspondence e-mail: ilona.turowska-tyrk@pwr.wroc.pl

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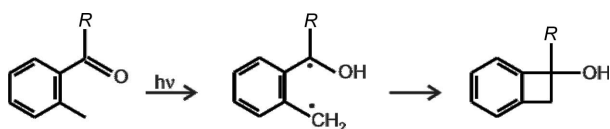
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The geometrical parameters governing the potential for the photocyclization reaction occurring in crystals of 2,3,4,5,6-pentamethylbenzophenone,  $C_{18}H_{20}O$ , (I), 1,3-diphenylbutan-1-one,  $C_{16}H_{16}O$ , (II), and 2,4,6-triisopropyl-4'-methoxybenzophenone,  $C_{23}H_{30}O_2$ , (IV), have been evaluated. Compound (IV) undergoes photocyclization but (I) and (II) do not, despite the fact that their geometrical parameters appear equally favourable for reaction. The structure of the partially reacted crystal of the photoactive compound, *i.e.* 2,4,6-triisopropyl-4'-methoxybenzophenone-3,5-diisopropyl-7-(4-methoxyphenyl)-8,8-dimethylbicyclo[4.2.0]octa-1,3,5-trien-7-ol (9/1),  $0.90C_{23}H_{30}O_2 \cdot 0.10C_{23}H_{30}O_2$ , (III), was also determined, providing structural evidence for the reactivity of the compound. It has been found that the carbonyl group of the photoactive compound reacts with one of the two *o*-isopropyl groups. The study has shown that the intramolecular geometrical parameters are not the only factors influencing the reactivity of compounds in crystals.

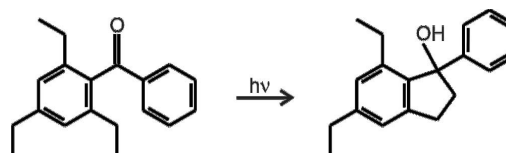
## Comment

Compounds containing a carbonyl group and an  $H\gamma$  atom can potentially undergo a photocyclization reaction. *ortho*-Alkylphenyl ketones are an example of such compounds. A mechanism of this reaction is presented in the scheme below (hereafter referred to as Scheme 1).



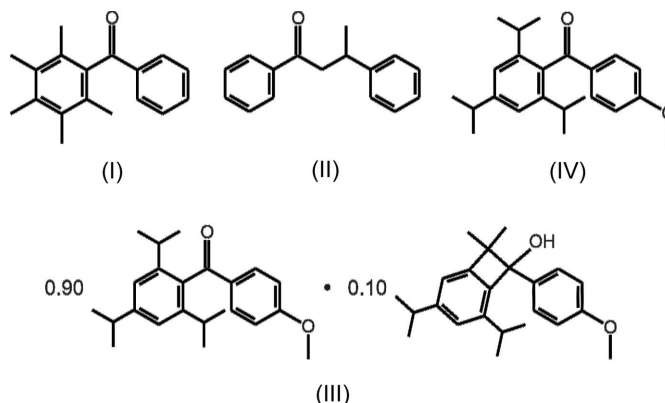
As can be seen, the reaction leads to the formation of a cyclobutane ring from a biradical formed previously under the

influence of UV-vis radiation. However, it has also been proposed that the mechanism of formation of benzocyclobutenols can have a more complicated character, namely the reaction can proceed not only *via* a biradical directly but, additionally, *via* an enol form (Ito *et al.*, 2009). Nevertheless, it was stated that, in the case of large substituents and steric crowding, formation of enols in a crystalline state can be neglected (Ito *et al.*, 2009; Moorthy *et al.*, 2004). *ortho*-Alkylphenyl ketones can also undergo a  $\delta$ -abstraction reaction (Ito *et al.*, 2009) as follows:



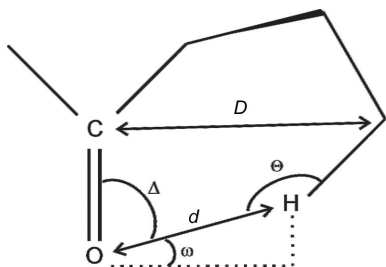
Some 2,4,6-triisopropylbenzophenones are photoactive in the crystalline state and undergo the photocyclization reaction according to Scheme 1 (Fukushima *et al.*, 1998; Ito *et al.*, 2009; Ito, Kano *et al.*, 1998). However, some 2,4,6-triisopropylbenzophenones are photoinert (Fukushima *et al.*, 1998; Ito, Kano *et al.*, 1998; Ito, Yasui *et al.*, 1998). Moreover, 2,4,6-trimethylbenzophenone is photoinert in the crystalline state (Ito *et al.*, 2009), but mesitylaldehyde in a solid inclusion compound is photoactive (Moorthy *et al.*, 2001).

In this paper, we present and discuss the structures of the following compounds: 2,3,4,5,6-pentamethylbenzophenone, (I), 1,3-diphenylbutan-1-one, (II), and 2,4,6-triisopropyl-4'-methoxybenzophenone-3,5-diisopropyl-7-(4-methoxyphenyl)-8,8-dimethylbicyclo[4.2.0]octa-1,3,5-trien-7-ol (9/1), (III), which is the product of the photocyclization of 2,4,6-triisopropyl-4'-methoxybenzophenone, (IV) (see Scheme 1). The intramolecular photocyclization is one of the reactions monitored by us recently (Turowska-Tyrk, Bąkiewicz *et al.*, 2006; Turowska-Tyrk, Bąkiewicz *et al.*, 2007; Turowska-Tyrk, Łabęcka *et al.*, 2007; Turowska-Tyrk, Trzop *et al.*, 2006).



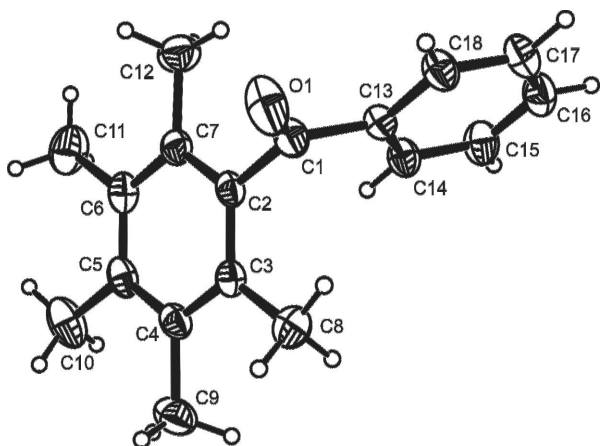
There exist geometrical parameters describing conditions that must be fulfilled for a photocyclization reaction to proceed in crystals (Natarajan *et al.*, 2005; Xia *et al.*, 2005). They are as follows (see the scheme below): the  $(C)O \cdots H\gamma$

distance,  $d$ , the (O)C...C $\gamma$  distance,  $D$ , the deviation of H $\gamma$  from the mean plane of the carbonyl group,  $\omega$ , the C=O...H $\gamma$  angle,  $\Delta$ , and the C $\gamma$ —H $\gamma$ ...O angle,  $\Theta$ . The ideal and average literature values of these parameters for photoactive compounds are given in Table 1. However, it should be pointed out that good values of these parameters are not the only necessary condition for photocyclization to proceed in crystals (Bąkiewicz & Turowska-Tyrk, 2009; Ito, Yasui *et al.*, 1998; Moorthy *et al.*, 2006; Zouev *et al.*, 2006).



One of the reasons for photochemical inactivity of compounds can be the presence of intermolecular  $\pi$ – $\pi$  interactions. They hinder shifts of atoms and in this manner a whole reaction (Fukushima *et al.*, 1998; Ito *et al.*, 2009). Too small a reaction cavity can be another reason for photochemical inactivity (Fukushima *et al.*, 1998; Ito, Kano *et al.*, 1998; Ito, Yasui *et al.*, 1998; Moorthy *et al.*, 2006; Zouev *et al.*, 2006). In these cases, despite the formation of biradicals, compounds do not cyclize but return to substrates (Ito, Yasui *et al.*, 1998). In order to make molecular and atomic movements easier, reactions were sometimes conducted at elevated temperatures (Fukushima *et al.*, 1998; Ito, Yasui *et al.*, 1998).

Figs. 1 and 2 present the structures of (I) and (II), respectively. The bond lengths in the molecules of both compounds are typical. The dihedral angles between the planes of the two benzene rings are 82.98 (5) and 62.36 (10)° for (I) and (II), respectively. The above-mentioned geometrical parameters influencing the photochemical reaction of the title compounds



**Figure 1**  
The molecular structure of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level.

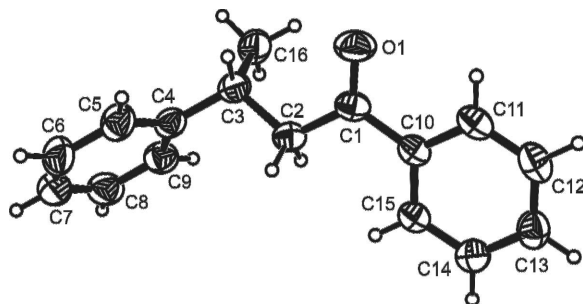
are given in Table 1. In the case of (I) and (II), only the values for the H $\gamma$  atom closer to the carbonyl group are given, but for (IV), the values for both *o*-isopropyl groups are presented. As can be seen, not all of the geometrical parameters for (I), (II) and (IV) are appropriate for the photocyclization reaction in crystals. For (I), the value of the  $\omega$  parameter is greater (by 10.5°) than the largest literature value for compounds undergoing the Yang photocyclization (Turowska-Tyrk, Bąkiewicz *et al.*, 2007). In the case of (II),  $D$  is slightly worse (by 0.02 Å) than the limit known in the literature, but  $\omega$  is slightly better (by 3.8°). For the first *o*-isopropyl group of (IV), the  $d$  and  $\omega$  parameters are larger and exceed the literature values (by 0.13 Å and 15.6°, respectively). For the second *o*-isopropyl group,  $d$ ,  $\omega$  and  $\Theta$  are worse (by 0.05 Å, 10.9° and 0.7°, respectively).

In the case of (I)–(III), there are no  $\pi$ – $\pi$  interactions between neighbouring naphthalene rings. The lack of  $\pi$ – $\pi$  stacking can increase the reactivity of compounds (Fukushima *et al.*, 1998; Ito *et al.*, 2009).

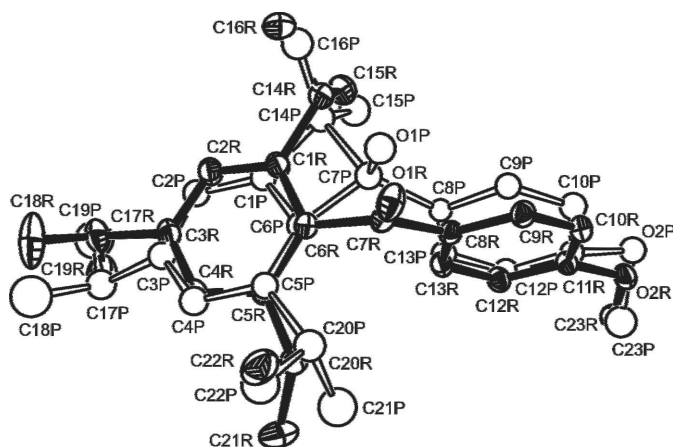
However, despite the above considerations, (I) and (II) are photoinert and (IV) photoactive. Irradiation of crystals of (I) and (II) for periods of 7 and 6 h, respectively, did not cause the photocyclization reaction. We did not observe any changes in the cell constants over the irradiation time and the structures determined after the irradiation revealed only reactant molecules.

In order to make the photoreaction easier, (I) (m.p. 410–411 K) and (II) (m.p. 343–345 K) were irradiated at elevated temperatures: at 373 K for 4 h and at 313 K for 5 h, respectively. Nevertheless, it did not help to induce the photoreaction.

The structure of (IV) before irradiation, *i.e.* containing only reactant molecules, has been reported previously (Fukushima *et al.*, 1998). Nevertheless, we redetermined it in order to have confidence that we have the proper structure for further experiments. The molecular geometries for both structures were very similar. The information that (IV) undergoes the photocyclization reaction according to Scheme 1 was also given previously (Fukushima *et al.*, 1998; Ito & Matura, 1988), but structural evidence, *i.e.* a structure of a crystal containing product molecules, was not supplied. The photoreaction of (IV) does not proceed in a single-crystal-to-single-crystal manner. Crystals under prolonged influence of UV–vis



**Figure 2**  
The molecular structure of (II), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level.

**Figure 3**

A view of the photoproduct molecule (empty bonds) superimposed on the reactant molecule (filled bonds) for the crystal of (III). H atoms have been omitted for clarity. Displacement ellipsoids are drawn at the 10% probability level.

radiation lose their diffracting properties. Nevertheless, we were able to determine the crystal structure containing 89.6 (7)% of reactant and 10.4 (7)% of product molecules. The structure is presented in Fig. 3. It is very interesting that the carbonyl group reacts with one of two *o*-isopropyl groups, at least at the beginning of the photoreaction. Unfortunately, because the crystal loses its diffracting properties, it is not possible to see the behaviour of the compound during the rest of the photoreaction.

In many cases, intramolecular parameters describing geometrical demands for a chemical reaction work very well. In the scientific literature, many such examples are known (for instance: Chen *et al.*, 2005; Ihmels & Scheffer, 1999; Leibovitch *et al.*, 1998; Natarajan *et al.*, 2005; Turowska-Tyrk, Bąkowicz *et al.*, 2007; Turowska-Tyrk, Łabęcka *et al.*, 2007; Turowska-Tyrk, Trzop *et al.*, 2006; Vishnumurthy *et al.*, 2002; Xia *et al.*, 2005). However, there are also situations where predictions about reactivity on the basis of such parameters fail (for instance: Fukushima *et al.*, 1998; Ito, Kano *et al.*, 1998). Such a situation concerns also the title compounds.

## Experimental

Compounds (I) and (II) were purchased from Alfa Aesar and compound (IV) from Sigma–Aldrich. Compounds (I) and (II) were recrystallized from acetone and ethanol, respectively; (IV) was not recrystallized.

### Compound (I)

#### Crystal data

$C_{18}H_{20}O$	$V = 1458.1 (6) \text{ \AA}^3$
$M_r = 252.34$	$Z = 4$
Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation
$a = 6.3784 (15) \text{ \AA}$	$\mu = 0.07 \text{ mm}^{-1}$
$b = 12.793 (2) \text{ \AA}$	$T = 299 \text{ K}$
$c = 18.014 (5) \text{ \AA}$	$0.60 \times 0.30 \times 0.13 \text{ mm}$
$\beta = 97.28 (2)^\circ$	

**Table 1**

Values of geometrical parameters describing photocyclization.

	$d$ (Å)	$D$ (Å)	$\omega$ (°)	$\Delta$ (°)	$\Theta$ (°)
Ideal value	< 2.7		0	90–120	180
Average literature value <sup>a</sup>	2.64 (8)	3.00 (9)	54 (10)	82 (8)	116 (3)
Range <sup>b</sup>	2.49–2.82	2.82–3.12	49.0–67.5	52.9–88.0	111.0–128.0
(I) (this work)	2.71	2.885 (3)	78.0	61.5	121.8
(II) (this work)	2.58	3.142 (4)	45.2	87.6	117.8
(IV) <sup>c</sup>	2.95	2.931 (5)	83.1	53.5	122.8
	2.89	2.928 (5)	77.9	58.5	108.9

Notes: (a) the mean values of  $d$ ,  $\omega$  and  $\Delta$  are given for 57 and  $\Theta$  for 40 aromatic ketones undergoing photocyclization (Natarajan *et al.*, 2005), and  $D$  for 53 structures (Xia *et al.*, 2005); (b) the range of the parameters is given on the grounds of 47 compounds for  $d$ ,  $\omega$ ,  $\Delta$  and  $\Theta$  (Chen *et al.*, 2005; Ihmels & Scheffer, 1999; Leibovitch *et al.*, 1998; Natarajan *et al.*, 2005; Turowska-Tyrk, Bąkowicz *et al.*, 2007; Turowska-Tyrk, Łabęcka *et al.*, 2007; Turowska-Tyrk, Trzop *et al.*, 2006; Vishnumurthy *et al.*, 2002) and 15 compounds for  $D$  (Leibovitch *et al.*, 1998; Turowska-Tyrk, Bąkowicz *et al.*, 2007; Turowska-Tyrk, Łabęcka *et al.*, 2007; Turowska-Tyrk, Trzop *et al.*, 2006); (c) on the basis of the literature data (Fukushima *et al.*, 1998) – the first and the second lines are for the reacting and unreacting isopropyl groups, respectively.

#### Data collection

Kuma KM-4 CCD diffractometer	1751 reflections with $I > 2\sigma(I)$
7742 measured reflections	$R_{\text{int}} = 0.036$
2553 independent reflections	

#### Refinement

$R[F^2 > 2\sigma(F^2)] = 0.057$	177 parameters
$wR(F^2) = 0.177$	H-atom parameters constrained
$S = 1.04$	$\Delta\rho_{\text{max}} = 0.17 \text{ e \AA}^{-3}$
2553 reflections	$\Delta\rho_{\text{min}} = -0.21 \text{ e \AA}^{-3}$

### Compound (II)

#### Crystal data

$C_{16}H_{16}O$	$V = 1261.4 (3) \text{ \AA}^3$
$M_r = 224.29$	$Z = 4$
Orthorhombic, $Pca2_1$	Mo $K\alpha$ radiation
$a = 10.7926 (18) \text{ \AA}$	$\mu = 0.07 \text{ mm}^{-1}$
$b = 14.931 (2) \text{ \AA}$	$T = 299 \text{ K}$
$c = 7.8275 (11) \text{ \AA}$	$0.30 \times 0.15 \times 0.10 \text{ mm}$

#### Data collection

Kuma KM-4 CCD diffractometer	1050 reflections with $I > 2\sigma(I)$
6471 measured reflections	$R_{\text{int}} = 0.029$
1201 independent reflections	

#### Refinement

$R[F^2 > 2\sigma(F^2)] = 0.038$	1 restraint
$wR(F^2) = 0.115$	H-atom parameters constrained
$S = 1.05$	$\Delta\rho_{\text{max}} = 0.11 \text{ e \AA}^{-3}$
1201 reflections	$\Delta\rho_{\text{min}} = -0.11 \text{ e \AA}^{-3}$
155 parameters	

### Compound (III)

#### Crystal data

$0.90C_{23}H_{30}O_2 \cdot 0.10C_{23}H_{30}O_2$	$V = 2093.7 (4) \text{ \AA}^3$
$M_r = 338.47$	$Z = 4$
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation
$a = 9.2288 (10) \text{ \AA}$	$\mu = 0.07 \text{ mm}^{-1}$
$b = 12.0541 (14) \text{ \AA}$	$T = 299 \text{ K}$
$c = 18.821 (2) \text{ \AA}$	$0.40 \times 0.30 \times 0.15 \text{ mm}$
$\beta = 90.021 (9)^\circ$	

# Data collection

Kuma KM-4 CCD diffractometer  
9964 measured reflections  
3564 independent reflections

1609 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.040$

# Refinement

$R[F^2 > 2\sigma(F^2)] = 0.066$   
 $wR(F^2) = 0.232$   
 $S = 1.00$   
3564 reflections  
328 parameters

224 restraints  
H-atom parameters constrained  
 $\Delta\rho_{\text{max}} = 0.26 \text{ e } \text{\AA}^{-3}$   
 $\Delta\rho_{\text{min}} = -0.15 \text{ e } \text{\AA}^{-3}$

Methyl H atoms of (I) and of the C23 methyl group of (III) were located in difference Fourier maps and refined as part of rigid rotating groups. The remaining H atoms of (I) and (III) and all H atoms of (II) were positioned geometrically and treated as riding. C—H distances were fixed at 0.93–0.98 Å and  $U_{\text{iso}}(\text{H})$  values were fixed at  $1.5U_{\text{eq}}(\text{C})$  for methyl H atoms and at  $1.2U_{\text{eq}}(\text{C})$  for other H atoms.

The crystal of (IV) was irradiated for 4 h using a 100 W Hg lamp equipped with a water filter. For (III), the first atoms of the minor component (product) were found in a difference Fourier map and the remaining atoms were located geometrically. The difference peaks were seen near one *o*-isopropyl group and not near the other. The major component (reactant) was refined anisotropically and the minor component was refined isotropically. H atoms in –OH and –OCH<sub>3</sub> groups of the minor component were omitted. The percentage of product molecules was determined by refinement of the site-occupation factor. The  $R_1$  value improved from 0.075 to 0.066 after inclusion of the minor component. Owing to a reactant–product disorder, which is always a feature of partially reacted crystals, the following weak restraints from *SHELXL97* (Sheldrick, 2008) were applied for the minor component: DFIX, DANG, FLAT and SIMU. The DFIX and DANG commands restrained bond lengths and valence angles to target values. The target values were taken from the structures of the pure reactant (IV) and the pure photoproduct of a similar compound. FLAT restrained some atoms to be coplanar. SIMU restrained the displacement parameters of atoms of the photoproduct.

For (II), the absolute structure could not be determined and an arbitrary choice was made for the enantiomer (C3-*R*) chosen for the asymmetric unit.

For all compounds, data collection: *CrysAlis CCD* (Oxford Diffraction, 2003); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2003); data reduction: *CrysAlis RED*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *SHELXL97*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: GZ3170). Services for accessing these data are described at the back of the journal.

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