Structures and Photoreactivities of 2,4,6-Triisopropylbenzophenones

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Abstract

Crystal structures of 2,4,6-triisopropylbenzophenone (I) and its ten derivatives have been determined: (II) 2,4,6triisopropyl-3'-methoxybenzophenone, (III) 3'-chloroformyl-2,4,6-triisopropylbenzophenone, (IV) methyl 3-(2,4,6-triisopropylbenzoyl)benzoate, (V) 2,4,6-triisopropyl-4'-methylbenzophenone, (VI) 4'-tert-butyl-2,4,6triisopropylbenzophenone, (VII) 2,4,6-triisopropyl-4'methoxybenzophenone, (VIII) 4-(2,4,6-triisopropylbenzoyl)benzoic acid, (IX) 4'-chloroformyl-2,4,6-triisopropylbenzophenone, (X) methyl 4-(2,4,6-triisopropylbenzoyl)benzoate and (XI) ethyl 4-(2,4,6-triisopropylbenzoyl)benzoate. The conformations of these molecules are essentially the same. The central carbonyl moiety is approximately coplanar with the 3'- or 4'substituted phenyl group and perpendicular to the triisopropylphenyl ring. The photostability of (IX) and (X) in the solid state is attributed to the narrow reaction cavity of the triisopropylphenylcarbonyl moiety, i.e. the intramolecular movements of isopropyl groups in the triisopropylphenyl plane toward the carbonyl C atom are suppressed by intermolecular close contacts. One of the barriers for the photocyclization of (IX) and (X) is caused by a dimeric structure in crystals through the π - π interaction, which is the result of having a polar methoxycarbonyl or chloroformyl group at position 4' of the phenyl ring.

1. Introduction

The photochemistry of 2,4,6-triisopropylbenzophenones has been previously investigated (Ito *et al.*, 1981, 1983, 1985). These compounds photocyclize efficiently into the corresponding benzocyclobutenols not only in solution but also in the solid state (Ito *et al.*, 1988). The powdered sample was placed between two Pyrex plates, which do not transmit UV light of wavelength shorter than 280 nm thus preventing the back-reaction, and irradiated with a 400 W high-pressure mercury lamp at 273 K in Ar. The conversion to the benzocyclobutenols was 100% for (II), (V), (VI) and (VII) in 2 h (Table 1). On the other hand, crystals of (IX) and (X) are

© 1998 International Union of Crystallography Printed in Great Britain – all rights reserved completely photostable, although they are photoreactive in solution. In order to clarify the steric factors for solidstate photocyclization, crystal structures of 2,4,6-triisopropylbenzophenone (I) and its 3'- or 4'-derivatives (II)–(XI) have been determined. The structure of (I) has been reported once before with relatively low accuracy (Takemoto *et al.*, 1983).



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Crystal data, experimental conditions and refinement details are listed in Table 2. Other common experimental conditions are described below. An absorption correction was made for the COCl derivatives (III) and (IX) by integration from crystal shape. The positional and anisotropic displacement parameters of non-H atoms were refined on |F| by full-matrix least squares. Hatom positions were calculated geometrically and a riding refinement was carried out (C–H and O–H distances 0.96 Å). Selected bond lengths and angles for (X), which has the highest accuracy among the 11 compounds, are listed in Table 3.†



2. Experimental

The benzophenone derivatives were synthesized as described previously (Ito *et al.*, 1985, and references therein). Solvents for recrystallization were methanol for (I), (II), (V) and (VI), hexane for (III), (IV) and (VII)–(X), and ethanol for (XI).

[†] Supplementary data for this paper are available from the IUCr electronic archives (Reference: OA0012). Services for accessing these data are described at the back of the journal.

Table 1. Photoreactivities of 2,4,6-triisopropyl-R-benzophenones in the solid state

Compound <i>R</i> Radiation time (h)† Conversion (%)‡	(I) H 4 100	(II) <i>m</i> -OMe 2 100	(III) <i>m</i> -COCI 4 35	(IV) <i>m</i> -COOMe 2 100§	(V) <i>p</i> -Me 2 100	(VI) <i>p</i> -C(CH ₃) ₃ 2 100
Compound R	(VII) n-OMe	(VII n-C	II) Ooh	(IX)	(X) n-COOMe	(XI)
Radiation time (h)†	$\frac{p}{2}$	4 p C	0011	4.5	10	4 p COOL(
Conversion (%)‡	100	28		0	0	76

 \dagger A powdered sample was placed between two Pyrex plates and irradiated with a 400 W high-pressure mercury lamp at 273 K in Ar. \ddagger The yield of the cyclobutenol was estimated from NMR and TLC. \$ By-product ~10%.

Table 2. Experimental details (I) (II) (III) (IV) (V) Crystal data Chemical formula C22H28O C23H30O2 C23H27ClO2 C24H30O3 C23H30O Chemical formula 308.46 338.49 370.92 366.5 322.49 weight Monoclinic Monoclinic Cell setting Monoclinic Monoclinic Monoclinic Space group $P2_{1}/n$ $P2_{1}/n$ $P2_{1}/c$ $P2_{1}/n$ $P2_1/n$ 10.765 (3) 10.915 (2) 11.274 (1) 10.789 (2) $\hat{a(A)}$ 13.293 (2) b (Å) 16.657 (2) 17.292 (4) 17.606 (2) 13.348 (2) 14.804 (2) 11.228 (4) c (Å) 8.944 (2) 11.629(1) 14.786(1) 13.528 (2) 90 α (°) 90 90 90 90 104.62(1) 93.09(1) 91.61 (3) 108.49 (1) 95.67 (1) β (°) γ (°) 90 90 90 90 90 $V(Å^3)$ 1977.5 (6) 2089.3 (11) 2119.4 (5) 2214.2 (4) 2090.7 (6) 4 4 Ζ 4 4 4 $D_x (\text{Mg m}^{-3})$ 1.036 1.076 1.163 1.099 1.025 Μο Κα Radiation type Μο Κα Μο Κα Μο Κα Μο Κα Wavelength (Å) 0.71073 0.71073 0.71073 0.71073 0.71073 No. of reflections 25 25 25 25 25 for cell parameters heta range (°) μ (mm⁻¹) 10 - 1510 - 1510 - 1510 - 1510 - 150.193 0.071 0.0610.067 0.06 Temperature (K) 297 293 293 293 293 Prism Crystal form Prism Prism Prism Prism $0.5 \times 0.5 \times 0.5$ $0.7 \times 0.5 \times 0.5$ $0.6 \times 0.5 \times 0.4$ $0.6 \times 0.5 \times 0.4$ $0.6 \times 0.6 \times 0.6$ Crystal size (mm) Colourless Crystal colour Colourless Colourless Colourless Colourless Data collection Diffractometer Rigaku AFC-5 Rigaku AFC-5 Rigaku AFC-5 Rigaku AFC-5 Rigaku AFC-5 Data collection θ – 2θ scans $\theta - 2\theta$ scans θ –2 θ scans $\theta - 2\theta$ scans θ -2 θ scans method Absorption None None Integration None None correction T_{\min} 0.781 _ _ _ T_{max} No. of measured 0.847 3475 3641 3895 3932 4105 reflections 3728 3486 3688 3895 3268 No. of independent reflections No. of observed 1941 2155 2353 1797 1692 reflections Criterion for $|F_o| > 3\sigma(|F_o|)$ observed reflections 0.019 0.020 0.016 0.010 0.011 $R_{\rm int}$ 25 25 25 22.5 25 θ_{\max} (°) $0 \rightarrow h \rightarrow 16$ $0 \rightarrow h \rightarrow 13$ $0 \rightarrow h \rightarrow 13$ $0 \rightarrow h \rightarrow 13$ $0 \rightarrow h \rightarrow 11$ Range of h, k, l $0 \to k \to 20$ $0 \to k \to 21$ $0 \to k \to 21$ $0 \to k \to 16$ $0 \rightarrow k \rightarrow 15$

2,4,6-TRIISOPROPYLBENZOPHENONES

	(I)	(II)	(III)	(IV)	(V)
	$-11 \rightarrow l \rightarrow 11$	$-13 \rightarrow l \rightarrow 13$	$-14 \rightarrow l \rightarrow 14$	$-18 \rightarrow l \rightarrow 18$	$-14 \rightarrow l \rightarrow 14$
No. of standard reflections	3	3	3	3	3
Frequency of standard reflec-	Every 100 reflec- tions				
Intensity decay (%)	0	0	0	0	1.8
Refinement					
Refinement on	F	F	F	F	F
R	0.072	0.066	0.074	0.077	0.074
wR	0.069	0.063	0.073	0.071	0.070
S No. of reflections used in refine- ment	1.21 1941	1.18 2155	1.32 2353	1.27 1797	1.23 1692
No. of parameters used	208	226	235	244	217
H-atom treatment Weighting scheme	H atoms riding $w = 1/[\sigma^2(F) + 0.0009F^2]$				
$(\Delta/\sigma)_{\rm max}$	0.01	0.01	0.002	0.01	0.01
$\Delta \rho_{\text{max}} (e A^{-3})$	0.22	0.18	0.21	0.21	0.17
$\Delta \rho_{\rm min}$ (e A ³)	-0.24	-0.20	-0.42	-0.25	-0.23
method	None	None	None	None	None
source of atomic scattering factors	International Tables for X- ray Crystallo- graphy (1974, Vol. IV)				
Computer					
Data collection	MSC/AFC (Mole- cular Structure Corporation, 1988)				
Cell refinement	MSC/AFC (Mole- cular Structure Corporation, 1988)				
Data reduction Structure solution	Local programs CRYSTAN-GM (Edwards et al.,				
Structure refine- ment	1995) CRYSTAN-GM (Edwards et al., 1995)	1995) CRYSTAN-GM (Edwards et al., 1995)	1995) CRYSTAN-GM (Edwards et al., 1995)	1995) CRYSTAN-GM (Edwards et al., 1995)	1995) CRYSTAN-GM (Edwards <i>et al.</i> , 1995)
Preparation of	CRYSTAN-GM	CRYSTAN-GM	CRYSTAN-GM	CRYSTAN-GM	CRYSTAN-GM
material for	(Edwards et al.,				
publication	1995)	1995)	1995)	1995)	1995)
	(VI)	(VII)	(VIII)	(IX)	(X)
Crystal data	A H A				A H C
Chemical formula Chemical formula weight	С ₂₆ н ₃₆ О 364.57	$C_{23}H_{30}O_2$ 338.49	C ₂₃ H ₂₈ O ₃ 352.47	C ₂₃ H ₂₇ ClO ₂ 370.92	$C_{24}H_{30}O_{3}$ 366.5
Cell setting	Monoclinic	Monoclinic	Triclinic	Orthorhombic	Triclinic
Space group	$P2_1/n$	$P2_1/c$	P1	Pcab	P1
$a(\mathbf{A})$ $b(\mathbf{A})$	10.033(2)	9.312 (2)	11./10(1) 15.010(2)	17.466(2)	8.679 (1)
$v(\mathbf{A})$	22.830 (2)	12.003 (2)	13.010 (2)	20.337 (2)	20.095 (5)

Table 2 (cont.)

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Table 2 (cont.)

	(VI)	(VII)	(VIII)	(IX)	(X)
c (Å)	11,227 (1)	18 804 (2)	6 224 (1)	11,749 (2)	6.160 (1)
α (°)	90	90	95.55(1)	90	93.96 (2)
$\beta(^{\circ})$	113.73 (1)	90.00 (1)	97.05(1)	90	103.14(2)
γ (°)	90	90	77.79(1)	90	78.22(1)
$V(A^3)$	2356.8 (6)	2102.1 (6)	1058.3 (2)	4214.4 (10)	1064.5(3)
Z	4	4	2	8	2
D (Mg m ⁻³)	1.027	1.070	-	1.169	1.143
Radiation type	Μο Κα	Μο Κα	Μο Κα	Μο Κα	Μο Κα
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073	0.71073
No. of reflections	25	25	25	25	25
for cell para-					
meters					
θ range (°)	10-15	12.9-14.6	10-15	10-15	10-15
$\mu \text{ (mm}^{-1})$	0.06	0.066	0.072	0.194	0.074
Temperature (K)	293	297	293	293	293
Crystal form	Prism	Prism	Prism	Prism	Prism
Crystal size (mm)	$0.5 \times 0.3 \times 0.3$	$0.7 \times 0.5 \times 0.2$	$0.6 \times 0.2 \times 0.2$	$0.6 \times 0.6 \times 0.6$	$0.7 \times 0.5 \times 0.5$
Crystal colour	Colourless	Colourless	Pale yellow	Pale yellow	Colourless
Data collection					
Diffractometer	Rigaku AFC-5	Rigaku AFC-5	Rigaku AFC-5	Rigaku AFC-5	Rigaku AFC-5
Data collection	ω scans	θ –2 θ scans	θ –2 θ scans	θ –2 θ scans	ω scans
method	N.	N.	N.	T	N.
Absorption	None	None	None	Integration	None
correction				0.900	
I _{min} T	_	_	_	0.899	_
I max No. of measured	-		- 3015	3600	- 4030
reflections	5557	3930	3913	3099	4050
No. of indepen-	3291	3705	3712	3699	3759
dent reflections	5271	5765	5712	5077	5155
No. of observed	1748	1911	2252	2030	2897
reflections					
Criterion for	$ F_{a} > 3\sigma(F_{a})$	$ F_{a} > 3\sigma(F_{a})$	$ F_{a} > 3\sigma(F_{a})$	$ F_{a} > 3\sigma(F_{a})$	$ F_a > 3\sigma(F_a)$
observed					
reflections					
R _{int}	0.016	0.015	0.010	-	0.011
$\theta_{\rm max}$ (°)	22.5	25	25	25	25
Range of h, k, l	$0 \rightarrow h \rightarrow 10$	$0 \rightarrow h \rightarrow 11$	$0 \rightarrow h \rightarrow 14$	$0 \rightarrow h \rightarrow 21$	$0 \rightarrow h \rightarrow 10$
	$0 \rightarrow k \rightarrow 24$	$0 \rightarrow k \rightarrow 14$	$-18 \rightarrow k \rightarrow 18$	$0 \rightarrow k \rightarrow 24$	$-25 \rightarrow k \rightarrow 25$
	$-12 \rightarrow l \rightarrow 12$	$-22 \rightarrow l \rightarrow 22$	$-7 \rightarrow l \rightarrow 7$	$0 \rightarrow l \rightarrow 14$	$-7 \rightarrow l \rightarrow 7$
No. of standard	3	3	3	3	3
renections	Examp 100 moffee	Excern 100 moffee	Every 100 reflee	Every 100 reflee	Exami 100 moffee
standard reflec	tions	Every 100 reliec-	Every 100 reliec-	Every 100 reliec-	Every 100 reliec-
tions	tions	tions	tions	tions	tions
Intensity decay	2	0	0	26	0
(%)	-	Ū.	0	210	0
Refinement	T.	r.	T.	T.	
Rennement on	F 0.081	r 0.072	r 0.069	ľ 0.076	F 0.052
л wP	0.081	0.072	0.008	0.070	0.052
wn c	0.075	0.000	0.004	0.009	1.05
No. of reflections	1.55	1.21	2252	2030	2807
used in refine-	1/10	1711	<i>LLJL</i>	2050	2077
ment					
No. of parameters	244	226	235	235	244
used					
H-atom treatment	H atoms riding	H atoms riding	H atoms riding	H atoms riding	H atoms riding
Weighting scheme	$w = 1/[\sigma^2(F) + $	$w = 1/[\sigma^2(F) + $	$w = 1/[\sigma^2(F) + $	$w = 1/[\sigma^2(F) + $	$w = 1/[\sigma^2(F) +$
	$0.0009F^2$]	$0.0009F^2$]	$0.0009F^2$]	$0.0009F^2$]	$0.0009F^2$]
$(\Delta/\sigma)_{\rm max}$	0.02	0.02	0.02	0.01	0.003

2,4,6-TRIISOPROPYLBENZOPHENONES

	(VI)		(VII)	(VIII)	(IX)		(X)
Λ_0 (e Å ⁻³)	0.21		0.26	0.20	0.23		0.17
$\Delta \rho_{\text{max}} (e \text{ Å}^{-3})$	-0.23		-0.18	-0.23	-0.2	5	-0.20
Extinction	None		None	None	None	e	None
method							
Source of atomic	Internation	nal	International	International	Inter	national	International
scattering	Tables j	tor X-	Tables for X-	Tables for X-	Ta	ibles for X-	Tables for X-
Tactors	oranhy	(1974	oranhy (1974	graphy (1974	ru or	anhy (1974	graphy (1974
	Vol. IV)	Vol. IV)	Vol. IV)	Vo	ol. IV)	Vol. IV)
Computer							
Data collection	MSC/AFC	C (Mole-	MSC/AFC (Mole-	MSC/AFC (Mole-	MSC	VAFC (Mole-	MSC/AFC (Mole-
	cular St	ructure	cular Structure	cular Structure	cu	lar Structure	cular Structure
	Corpora	ation,	Corporation,	Corporation,	Co	orporation,	Corporation,
	1988)		1988)	1988)	19	88)	1988)
Cell refinement	MSC/AFC	(Mole-	MSC/AFC (Mole-	MSC/AFC (Mole-	MSC	/AFC (Mole-	MSC/AFC (Mole-
	Corpor	ation	Corporation	Corporation	Cu	orporation	Corporation
	1988)	ation,	1988)	1988)	19	88)	1988)
Data reduction	Local prog	grams	Local programs	Local programs	Loca	l programs	Local programs
Structure solution	CRYSTAI	N-GM	CRYSTAN-GM	CRYSTAN-GM	CRY	STAN-GM	CRYSTAN-GM
and refinement	(Edward	ds <i>et al</i> .,	(Edwards <i>et al.</i> ,	(Edwards <i>et al.</i> ,	(E	dwards <i>et al.</i> ,	(Edwards <i>et al.</i> ,
Propagation of	1995) CRVSTAI	NCM	1995) CRVSTAN CM	1995) CRYSTAN CM	19 CPV	95) STANCM	1995) CRYSTAN CM
material for	(Edward	ds <i>et al</i>	(Edwards <i>et al</i>	(Edwards et al	(F	dwards <i>et al</i>	(Edwards <i>et al</i>
publication	1995)	us er un,	(1995)	(1995)	19	95)	(24 millius er um, 1995)
•							
		(XI)				(XI)	
Crystal data				Dance of h k l		0 > k > 12	
Chemical formula weight	rht	$C_{25}H_{32}O_3$		Kange of <i>n</i> , <i>k</i> , <i>i</i>		$0 \rightarrow n \rightarrow 12$ -15 $\rightarrow k \rightarrow 1^{\circ}$	5
Cell setting	5111	Triclinic				$-11 \rightarrow l \rightarrow 11$	
Space group		$P\overline{1}$		No. of standard reflections	3	3	
a (Å)		10.830 (2)		Frequency of standard refl	ections	Every 100 refle	ections
$b(\mathbf{A})$		12.717 (2)		Intensity decay (%)		4	
$c(\mathbf{A})$		9.379(1)		Refinement			
β (°)		99.15 (1)		Refinement on		F	
γ (°)		105.14 (1)		R		0.068	
$V(Å^3)$		1171.6 (3)		wR		0.072	
Z		2		S S	c	1.16	
D_x (Mg m ⁻³) Rediction type		1.079 Mo. Ko		No. of reflections used in a	renne-	2456	
Wavelength (Å)		0.71073		No. of parameters used		253	
No. of reflections for c	ell para-	25		H-atom treatment		H atoms riding	
meters	•			Weighting scheme		$w = 1/[\sigma^2(F) +$	$0.0009F^2$]
θ range (°)		10–15		$(\Delta/\sigma)_{\rm max}$		0.004	
$\mu (\text{mm}^{-1})$		0.069		$\Delta \rho_{\text{max}} (e A^{-3})$		0.24	
Crystal form		293 Prism		$\Delta \rho_{\rm min}$ (e A) Extinction method		-0.28 None	
Crystal size (mm)		$0.5 \times 0.4 \times$	0.4	Source of atomic scatterin	g	International T	ables for X-ray
Crystal colour		Colourless		factors	-	Crystallogra	ohy (1974, Vol. IV)
Data collection				Computer programs			
Diffractometer		Rigaku AF0	C-5	Data collection		MSC/AFC (Mc	blecular Structure
Data collection method	d	θ –2 θ scans				Corporation,	, 1988)
Absorption correction		None		Cell refinement		MSC/AFC	
No. of measured reflec	tions	4353		Data reduction		Local programs	S
No. of independent ref	lections	4115		Structure solution		CRYSTAN-GN 1005)	a (Edwards et al.,
Criterion for observed	reflections	$ F > 3\sigma(1)$	F)	Structure refinement		CRYSTAN-GA	1
R _{int}		0.013	017	Preparation of material fo	r	CRYSTAN-GM	1
θ_{\max} (°)		25		publication			

Table 2 (cont.)

Table 3. Selected geometric parameters (Å, $^{\circ}$) for (X)

	ē	•	
O1-C10	1.211 (2)	C8-C23	1.517 (2)
C4-C5	1.395 (2)	C9-C10	1.513 (2)
C4-C9	1.394 (2)	C10-C11	1.490(2)
C4-C17	1.520 (2)	C17-C18	1.516 (2)
C5-C6	1.378 (2)	C17-C19	1.512 (2)
C6-C7	1.383 (2)	C20-C21	1.509 (2)
C6-C20	1.518 (2)	C20-C22	1.507 (2)
C7-C8	1.388 (2)	C23-C24	1.516 (2)
C8-C9	1.394 (2)	C23-C25	1.518 (2)
C5-C4-C9	118.0(1)	C8-C9-C10	119.0 (1)
C5-C4-C17	120.2 (1)	O1-C10-C9	120.3 (1)
C9-C4-C17	121.7 (1)	O1-C10-C11	120.1 (1)
C4-C5-C6	122.1 (1)	C9-C10-C11	119.6 (1)
C5-C6-C7	118.1 (1)	C4-C17-C18	110.5 (1)
C5-C6-C20	121.7 (1)	C4-C17-C19	112.1 (1)
C7-C6-C20	120.2 (1)	C18-C17-C19	110.6 (2)
C6-C7-C8	122.5 (1)	C6-C20-C21	110.5(1)
C7-C8-C9	117.8 (1)	C6-C20-C22	113.6 (1)
C7-C8-C23	121.0 (1)	C21-C20-C22	111.9 (1)
C9-C8-C23	121.2 (1)	C8-C23-C24	113.2 (1)
C4-C9-C8	121.5 (1)	C8-C23-C25	110.7 (1)
C4-C9-C10	119.5 (1)	C24-C23-C25	111.0 (1)
	. ,		

Although β is 90.00 (1)° for (VII), the Laue group is apparently not mmm, but 2/m. Rotational disorder of the isopropyl groups was observed in most of the compounds. As seen in Fig. 1, the ellipsoids of the isopropyl terminal C atoms are large and elongated. The split-atom model was tried for some compounds, but remarkable improvement of R values was not obtained. The average R value for the 11 compounds studied (0.052 < R < 0.081) was 0.071, which is rather high and may be due to the disorder of the substituents. In (IX) rotational disorder of the chloroformyl group was taken into account. The COCl group is almost coplanar with the phenyl ring and has two possible orientations. The split-atom model was not applicable to the present case owing to the overlapping of the diffuse electron densities of the disordered Cl and O atoms. By using the approximation that the positions of Cl and O in the orientation of Cl-C=O are the same as those of O and Cl in the other orientation of O = C - Cl, and assuming that the probabilities of the two orientations are 50% each, the artificial occupancy factors of Cl1 and O3 atoms were estimated to be $(17 \times 0.5 + 8 \times 0.5)/17$ and $(17 \times 0.5 + 8 \times 0.5)/8$, respectively, based on the number of electrons of the elements, following the treatment of orientational disorder of thiophene rings (Pelletier & Brisse, 1994). The refined U_{eq} values of Cl1 and O3 positions were similar, 0.133 (1) and 0.121 (1) $Å^2$, indicating that the model of disorder is reasonable.

3. Discussion

3.1. Molecular structure

The conformations of the molecules are essentially the same for all the compounds, as shown in Fig. 1. The A is the triisopropylphenyl group and B the 3'- or 4'-substituted phenyl group. The standard uncertainties of the dihedral angles are $\sim 1^{\circ}$.

	φ_A	φ_B
(I)	86.4	3.5
(II)	78.5	5.1
(III)	88.6	11.1
(IV)	87.2	7.4
(V)	88.5	9.7
(VI)	80.8	7.5
(VII)	81.8	14.8
(VIII)	83.7	5.5
(IX)	86.4	6.8
(X)	89.0	8.1
(XI)	87.2	9.1

carbonyl plane is almost perpendicular to the triisopropylphenyl ring, the dihedral angle φ_A being 79 (1)– 89 (1) $^{\circ}$ (Table 4). The methine H atoms of the isopropyl groups at positions 2 and 6 are directed towards the carbonyl side, as the result of minimizing the steric repulsions between the neighbouring substituents. The distances between the isopropyl methine H and the carbonyl O atoms are 2.7-3.3 Å. Fig. 2 shows the variation of the intramolecular distances between the carbonyl O and the central C atoms of the orthoisopropyl groups along with the angle φ_A . The greater the deviation of φ_A from 90°, the shorter one of the $O \cdots C$ (isopropyl) distances becomes, which seems favourable for hydrogen abstraction by the excited carbonyl O atom in photoirradiation. Indeed, (II), (VI) and (VII) have $\varphi_A = 79 (1)-82 (1)^\circ$ and show high photoreactivity. However, the dihedral angle φ_A is not directly correlated with the reactivity, since φ_A of the other highly photoreactive compounds (IV) and (V) range between 87 (1) and 89 (1)°. There is an orientational disorder of the isopropyl group at position 4. Fig. 3 shows the correlation between the $C-CH_3$ bond distances and the CH₃-C-CH₃ bond angles. The shorter the C-CH₃ bond distances, which are artefact owing to the disorder, the larger the CH₃-C-CH₃ bond angle. In the photostable crystals (IX) and (X) there is a small degree of disorder, indicating a good efficiency of molecular packing.

3.2. Reaction cavity

Since the key factor for photoreactivity was not found in the molecular structures, the environment of the molecules in the crystals was analysed using the program *CAVITY* (Ohashi *et al.*, 1981). The reaction cavity for the triisopropylphenylcarbonyl moiety was calculated assuming that neighbouring atoms have spheres of radii greater than the corresponding van der Waals radii by 1.2 Å. The intramolecular 3'- or 4'-substituted phenyl group was treated as constituting barrier atoms to clarify





C22 CC10 C12 C1 C1: **Ø** 03 (III)







Fig. 1. The molecular structures of (I)–(XI) with displacement ellipsoids at the 20% probability level. H atoms are represented by circles of radii 0.1 Å.









(IX)

O3



Fig. 1 (cont.)

the shape of the cavity around the triisopropylphenyl group. In Fig. 4 sections of the reaction cavity parallel to the phenyl plane with a shift of 0.5–1.5 Å downward from the plane are shown for the photostable *p*-COOMe derivative (X) and the photoreactive 4'-(S)-methylphenylalaninocarbonyl derivative (XII), whose structure and crystal-to-crystal transformation will be reported in the following paper (Hosomi *et al.*, 1998). At the depth 0.5–1.5 Å there are terminal C atoms of isopropyl groups, C19 and C24 in (X), and C21 and C26 in (XII),



Fig. 2. Correlation between the dihedral angle (φ_A) in Table 4 and the intramolecular O(carbonyl) \cdots C(isopropyl central) distances. The broken lines are the regression lines for longer and shorter O \cdots C distances.



Fig. 3. Correlation between the CH₃-C-CH₃ bond angle and the average of the C-CH₃ bond distances for the isopropyl group at position 4. The broken line is the regression line.

and the carbonyl O atoms are located upwards from the planes in Fig. 4. In (X) the isopropyl terminal C19 and C24 atoms are near the wall of the reaction cavity and it seems that the isopropyl groups cannot approach the *ortho*-carbonyl group. In (XII) the photocyclization occurs with the isopropyl group involving C26, because the carbonyl O atom predominantly abstracts the nearer methine H atom. The reaction cavity of (XII) allows the movement of the isopropyl group toward the carbonyl C atom and the bond angle φ indicated in Fig. 4 changes from 120.8 (9) to 93.2 (10)° by the formation of a cyclobutenol ring (Hosomi *et al.*, 1998).

At elevated temperatures, (IX) and (X) photoreact in the solid state. This fact indicates that the thermal





expansions of the crystal lattice lead to wider reaction cavities, which allow the molecules to be photocyclized. For the powder of (X) the conversion is 54% by irradiation at 357 K for 10 h and the energy barrier was estimated to be 84 kJ mol^{-1} from the temperature effects on the photolysis (Ito *et al.*, 1998).

3.3. Molecular arrangement

The narrow reaction cavity of (IX) and (X) is partly the result of the dimeric structure in the crystal through π - π interactions. As seen in Fig. 5, (III) PhCOCl, (IX) PhCOCl and (X) PhCOOMe groups related by a centre of symmetry are close to each other and the polar chloroformyl or methoxycarbonyl group is overlapped with the phenyl group of the other molecule. The interplanar distances are 3.44–3.58 (2) Å. Within the dimeric structure of (IX) and (X), the short contact which defines the part of the reaction cavity around the *ortho*-isopropyl groups, as shown in Fig. 4, is C19···O3 (at 1 - x, -y, -1 - z) 3.79 (1) Å in (IX) and C24···O2 (at 1 - x, -y, 1 - z) 3.631 (2) Å in (X). In the 4'-COOEt













Fig. 5. The dimeric structures of (a) (III), (b) (IX), (c) (X) and (d) (XI), through the π - π interactions. Projections in two directions are shown. Symmetry operations: (III) -x, -y, 1 - z; (IX) 1 - x, -y, -1 - z; (X) 1 - x, -y, 1 - z; (XI) 1 - x, 1 - y, 2 - z.

derivative (XI) these π - π interactions also exist, but the phenyl planes are slipped aside, which may be the result of the crystal packing force. The 3'-COOMe derivative (IV) does not have a dimeric structure in the crystal. In (VIII) a cyclic hydrogen bond is formed by the carboxylic groups related by a centre of symmetry and there is no π - π close contact.

4. Conclusions

Generally, 2,4,6-triisopropylbenzophenones photocyclize efficiently in the solid state. However, the 4'-COOMe and 4'-COCl derivatives do not show photoreactivity, which may be due to the environment of the molecules in the crystals. Steric repulsions of the neighbouring molecules lock the intramolecular movement of the isopropyl groups toward the carbonyl C atom. Part of the barrier for photoreaction is caused by the intermolecular π - π close contacts between PhCOOMe and between PhCOCl groups.

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