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Structures and Photoreactivities of 2,4,6-Triisopropylbenzophenones

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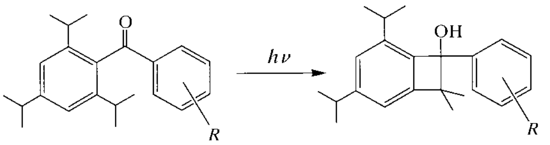
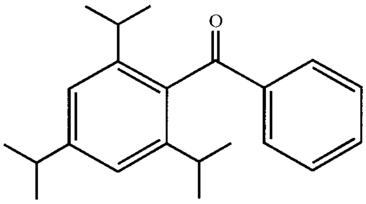
Abstract

Crystal structures of 2,4,6-triisopropylbenzophenone (I) and its ten derivatives have been determined: (II) 2,4,6-triisopropyl-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-2,4,6-triisopropylbenzophenone, (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 completely photostable, although they are photoreactive in solution. In order to clarify the steric factors for solid-state 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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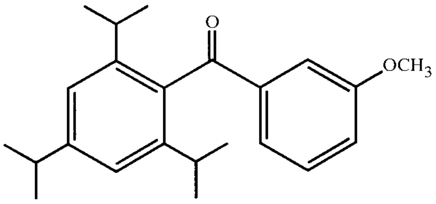
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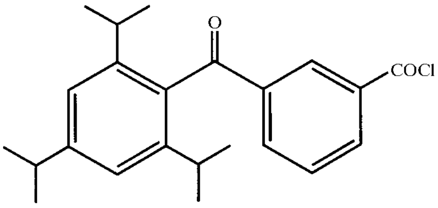
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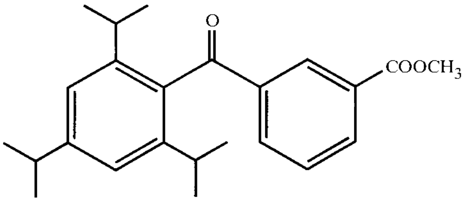

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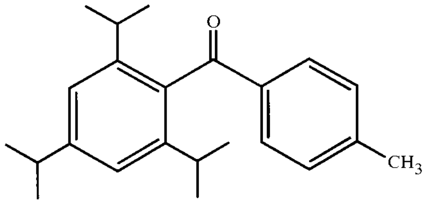

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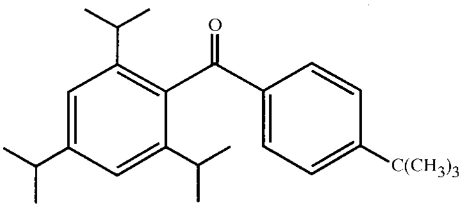

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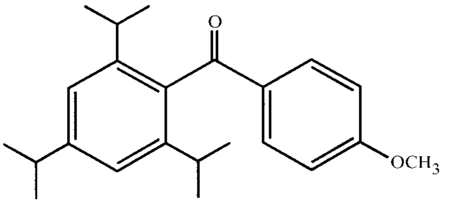
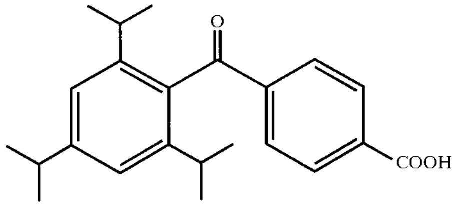


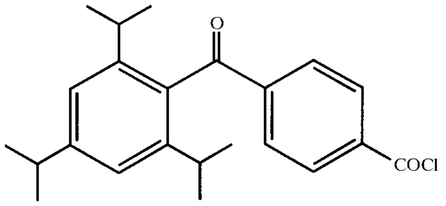
(VII)

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).



(VIII)



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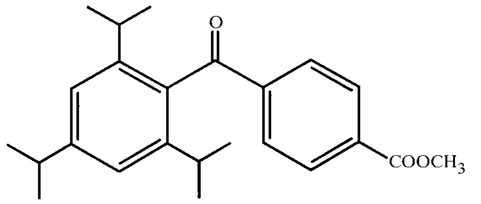
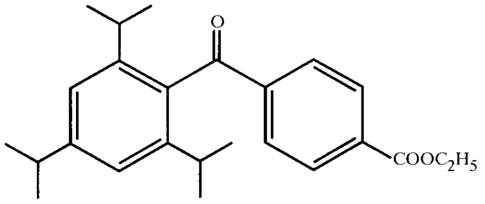


(X)



(XI)

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. H-atom 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.†

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† 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)	(II)	(III)	(IV)	(V)	(VI)
R	H	*m*-OMe	*m*-COCl	*m*-COOMe	*p*-Me	*p*-C(CH$_3$)$_3$
Radiation time (h)†	4	2	4	2	2	2
Conversion (%)‡	100	100	35	100§	100	100

Compound	(VII)	(VIII)	(IX)	(X)	(XI)
R	*p*-OMe	*p*-COOH	*p*-COCl	*p*-COOMe	*p*-COOEt
Radiation time (h)†	2	4	4.5	10	4
Conversion (%)‡	100	28	0	0	76

† A powdered sample was placed between two Pyrex plates and irradiated with a 400 W high-pressure mercury lamp at 273 K in Ar. ‡ 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	$C_{22}H_{28}O$	$C_{23}H_{30}O_2$	$C_{23}H_{27}ClO_2$	$C_{24}H_{30}O_3$	$C_{23}H_{30}O$
Chemical formula weight	308.46	338.49	370.92	366.5	322.49
Cell setting	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/n$	$P2_1/c$	$P2_1/n$	$P2_1/n$
a (Å)	13.293 (2)	10.765 (3)	10.915 (2)	11.274 (1)	10.789 (2)
b (Å)	16.657 (2)	17.292 (4)	17.606 (2)	13.348 (2)	14.804 (2)
c (Å)	8.944 (2)	11.228 (4)	11.629 (1)	14.786 (1)	13.528 (2)
α (°)	90	90	90	90	90
β (°)	93.09 (1)	91.61 (3)	108.49 (1)	95.67 (1)	104.62 (1)
γ (°)	90	90	90	90	90
V (Å^3)	1977.5 (6)	2089.3 (11)	2119.4 (5)	2214.2 (4)	2090.7 (6)
Z	4	4	4	4	4
D_x (Mg m^{-3})	1.036	1.076	1.163	1.099	1.025
Radiation type	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073	0.71073
No. of reflections for cell parameters	25	25	25	25	25
θ range (°)	10–15	10–15	10–15	10–15	10–15
μ (mm^{-1})	0.061	0.067	0.193	0.071	0.06
Temperature (K)	297	293	293	293	293
Crystal form	Prism	Prism	Prism	Prism	Prism
Crystal size (mm)	0.5 × 0.5 × 0.5	0.7 × 0.5 × 0.5	0.6 × 0.5 × 0.4	0.6 × 0.5 × 0.4	0.6 × 0.6 × 0.6
Crystal colour	Colourless	Colourless	Colourless	Colourless	Colourless
Data collection					
Diffractometer	Rigaku AFC-5	Rigaku AFC-5	Rigaku AFC-5	Rigaku AFC-5	Rigaku AFC-5
Data collection method	θ–2θ scans	θ–2θ scans	θ–2θ scans	θ–2θ scans	θ–2θ scans
Absorption correction	None	None	Integration	None	None
T_{min}	–	–	0.781	–	–
T_{max}	–	–	0.847	–	–
No. of measured reflections	3641	3895	3932	4105	3475
No. of independent reflections	3486	3688	3728	3895	3268
No. of observed reflections	1941	2155	2353	1797	1692
Criterion for observed reflections	$\|F_o\| > 3\sigma(\|F_o\|)$	$\|F_o\| > 3\sigma(\|F_o\|)$	$\|F_o\| > 3\sigma(\|F_o\|)$	$\|F_o\| > 3\sigma(\|F_o\|)$	$\|F_o\| > 3\sigma(\|F_o\|)$
R_{int}	0.019	0.020	0.016	0.010	0.011
θ_{max} (°)	25	25	25	25	22.5
Range of *h*, *k*, *l*	$0 \rightarrow h \rightarrow 16$ $0 \rightarrow k \rightarrow 20$	$0 \rightarrow h \rightarrow 13$ $0 \rightarrow k \rightarrow 21$	$0 \rightarrow h \rightarrow 13$ $0 \rightarrow k \rightarrow 21$	$0 \rightarrow h \rightarrow 13$ $0 \rightarrow k \rightarrow 16$	$0 \rightarrow h \rightarrow 11$ $0 \rightarrow k \rightarrow 15$

Table 2 (*cont.*)

	(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 reflections	Every 100 reflections	Every 100 reflections	Every 100 reflections	Every 100 reflections	Every 100 reflections
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	1.21	1.18	1.32	1.27	1.23
No. of reflections used in refinement	1941	2155	2353	1797	1692
No. of parameters used	208	226	235	244	217
H-atom treatment	H atoms riding	H atoms riding	H atoms riding	H atoms riding	H atoms riding
Weighting scheme	$w = 1/[\sigma^2(F) + 0.0009F^2]$	$w = 1/[\sigma^2(F) + 0.0009F^2]$	$w = 1/[\sigma^2(F) + 0.0009F^2]$	$w = 1/[\sigma^2(F) + 0.0009F^2]$	$w = 1/[\sigma^2(F) + 0.0009F^2]$
$(\Delta/\sigma)_{\max}$	0.01	0.01	0.002	0.01	0.01
$\Delta\rho_{\max}$ (e Å^{-3})	0.22	0.18	0.21	0.21	0.17
$\Delta\rho_{\min}$ (e Å^{-3})	−0.24	−0.20	−0.42	−0.25	−0.23
Extinction method	None	None	None	None	None
Source of atomic scattering factors	*International Tables for X-ray Crystallography* (1974, Vol. IV)	*International Tables for X-ray Crystallography* (1974, Vol. IV)	*International Tables for X-ray Crystallography* (1974, Vol. IV)	*International Tables for X-ray Crystallography* (1974, Vol. IV)	*International Tables for X-ray Crystallography* (1974, Vol. IV)
Computer programs					
Data collection	*MSC/AFC* (Molecular Structure Corporation, 1988)	*MSC/AFC* (Molecular Structure Corporation, 1988)	*MSC/AFC* (Molecular Structure Corporation, 1988)	*MSC/AFC* (Molecular Structure Corporation, 1988)	*MSC/AFC* (Molecular Structure Corporation, 1988)
Cell refinement	*MSC/AFC* (Molecular Structure Corporation, 1988)	*MSC/AFC* (Molecular Structure Corporation, 1988)	*MSC/AFC* (Molecular Structure Corporation, 1988)	*MSC/AFC* (Molecular Structure Corporation, 1988)	*MSC/AFC* (Molecular Structure Corporation, 1988)
Data reduction	Local programs	Local programs	Local programs	Local programs	Local programs
Structure solution	*CRYSTAN-GM* (Edwards *et al.*, 1995)	*CRYSTAN-GM* (Edwards *et al.*, 1995)	*CRYSTAN-GM* (Edwards *et al.*, 1995)	*CRYSTAN-GM* (Edwards *et al.*, 1995)	*CRYSTAN-GM* (Edwards *et al.*, 1995)
Structure refinement	*CRYSTAN-GM* (Edwards *et al.*, 1995)	*CRYSTAN-GM* (Edwards *et al.*, 1995)	*CRYSTAN-GM* (Edwards *et al.*, 1995)	*CRYSTAN-GM* (Edwards *et al.*, 1995)	*CRYSTAN-GM* (Edwards *et al.*, 1995)
Preparation of material for publication	*CRYSTAN-GM* (Edwards *et al.*, 1995)	*CRYSTAN-GM* (Edwards *et al.*, 1995)	*CRYSTAN-GM* (Edwards *et al.*, 1995)	*CRYSTAN-GM* (Edwards *et al.*, 1995)	*CRYSTAN-GM* (Edwards *et al.*, 1995)

	(VI)	(VII)	(VIII)	(IX)	(X)
Crystal data					
Chemical formula	$C_{26}H_{36}O$	$C_{23}H_{30}O_2$	$C_{23}H_{28}O_3$	$C_{23}H_{27}ClO_2$	$C_{24}H_{30}O_3$
Chemical formula weight	364.57	338.49	352.47	370.92	366.5
Cell setting	Monoclinic	Monoclinic	Triclinic	Orthorhombic	Triclinic
Space group	$P2_1/n$	$P2_1/c$	$P\bar{1}$	$Pcab$	$P\bar{1}$
a (Å)	10.033 (2)	9.312 (2)	11.710 (1)	17.466 (2)	8.679 (1)
b (Å)	22.856 (2)	12.005 (2)	15.010 (2)	20.537 (2)	20.893 (3)

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)
β (°)	113.73 (1)	90.00 (1)	97.05 (1)	90	103.14 (2)
γ (°)	90	90	77.79 (1)	90	78.22 (1)
V (Å^3)	2356.8 (6)	2102.1 (6)	1058.3 (2)	4214.4 (10)	1064.5 (3)
Z	4	4	2	8	2
D_x (Mg m^{-3})	1.027	1.070	1.106	1.169	1.143
Radiation type	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073	0.71073
No. of reflections for cell parameters	25	25	25	25	25
θ range (°)	10–15	12.9–14.6	10–15	10–15	10–15
μ (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 × 0.3 × 0.3	0.7 × 0.5 × 0.2	0.6 × 0.2 × 0.2	0.6 × 0.6 × 0.6	0.7 × 0.5 × 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 method	ω scans	θ–2θ scans	θ–2θ scans	θ–2θ scans	ω scans
Absorption correction	None	None	None	Integration	None
$T_{\min}$	–	–	–	0.899	–
$T_{\max}$	–	–	–	0.907	–
No. of measured reflections	3539	3950	3915	3699	4030
No. of independent reflections	3291	3705	3712	3699	3759
No. of observed reflections	1748	1911	2252	2030	2897
Criterion for observed reflections	$\|F_o\| > 3\sigma(\|F_o\|)$	$\|F_o\| > 3\sigma(\|F_o\|)$	$\|F_o\| > 3\sigma(\|F_o\|)$	$\|F_o\| > 3\sigma(\|F_o\|)$	$\|F_o\| > 3\sigma(\|F_o\|)$
$R_{\rm int}$	0.016	0.015	0.010	–	0.011
$\theta_{\max}$ (°)	22.5	25	25	25	25
Range of h, k, l	$0 \rightarrow h \rightarrow 10$ $0 \rightarrow k \rightarrow 24$ $-12 \rightarrow l \rightarrow 12$	$0 \rightarrow h \rightarrow 11$ $0 \rightarrow k \rightarrow 14$ $-22 \rightarrow l \rightarrow 22$	$0 \rightarrow h \rightarrow 14$ $-18 \rightarrow k \rightarrow 18$ $-7 \rightarrow l \rightarrow 7$	$0 \rightarrow h \rightarrow 21$ $0 \rightarrow k \rightarrow 24$ $0 \rightarrow l \rightarrow 14$	$0 \rightarrow h \rightarrow 10$ $-25 \rightarrow k \rightarrow 25$ $-7 \rightarrow l \rightarrow 7$
No. of standard reflections	3	3	3	3	3
Frequency of standard reflections	Every 100 reflections	Every 100 reflections	Every 100 reflections	Every 100 reflections	Every 100 reflections
Intensity decay (%)	2	0	0	2.6	0
Refinement					
Refinement on	F	F	F	F	F
R	0.081	0.072	0.068	0.076	0.052
wR	0.075	0.066	0.064	0.069	0.056
S	1.33	1.21	1.08	1.40	1.05
No. of reflections used in refinement	1748	1911	2252	2030	2897
No. of parameters used	244	226	235	235	244
H-atom treatment	H atoms riding	H atoms riding	H atoms riding	H atoms riding	H atoms riding
Weighting scheme	$w = 1/[\sigma^2(F) + 0.0009F^2]$	$w = 1/[\sigma^2(F) + 0.0009F^2]$	$w = 1/[\sigma^2(F) + 0.0009F^2]$	$w = 1/[\sigma^2(F) + 0.0009F^2]$	$w = 1/[\sigma^2(F) + 0.0009F^2]$
$(\Delta/\sigma)_{\max}$	0.02	0.02	0.02	0.01	0.003

Table 2 (*cont.*)

	(VI)	(VII)	(VIII)	(IX)	(X)
$\Delta\rho_{\max}$ (e Å^{-3})	0.21	0.26	0.20	0.23	0.17
$\Delta\rho_{\min}$ (e Å^{-3})	−0.23	−0.18	−0.23	−0.25	−0.20
Extinction method	None	None	None	None	None
Source of atomic scattering factors	*International Tables for X-ray Crystallography* (1974, Vol. IV)	*International Tables for X-ray Crystallography* (1974, Vol. IV)	*International Tables for X-ray Crystallography* (1974, Vol. IV)	*International Tables for X-ray Crystallography* (1974, Vol. IV)	*International Tables for X-ray Crystallography* (1974, Vol. IV)
Computer programs					
Data collection	*MSC/AFC* (Molecular Structure Corporation, 1988)	*MSC/AFC* (Molecular Structure Corporation, 1988)	*MSC/AFC* (Molecular Structure Corporation, 1988)	*MSC/AFC* (Molecular Structure Corporation, 1988)	*MSC/AFC* (Molecular Structure Corporation, 1988)
Cell refinement	*MSC/AFC* (Molecular Structure Corporation, 1988)	*MSC/AFC* (Molecular Structure Corporation, 1988)	*MSC/AFC* (Molecular Structure Corporation, 1988)	*MSC/AFC* (Molecular Structure Corporation, 1988)	*MSC/AFC* (Molecular Structure Corporation, 1988)
Data reduction	Local programs	Local programs	Local programs	Local programs	Local programs
Structure solution and refinement	*CRYSTAN-GM* (Edwards *et al.*, 1995)	*CRYSTAN-GM* (Edwards *et al.*, 1995)	*CRYSTAN-GM* (Edwards *et al.*, 1995)	*CRYSTAN-GM* (Edwards *et al.*, 1995)	*CRYSTAN-GM* (Edwards *et al.*, 1995)
Preparation of material for publication	*CRYSTAN-GM* (Edwards *et al.*, 1995)	*CRYSTAN-GM* (Edwards *et al.*, 1995)	*CRYSTAN-GM* (Edwards *et al.*, 1995)	*CRYSTAN-GM* (Edwards *et al.*, 1995)	*CRYSTAN-GM* (Edwards *et al.*, 1995)

	(XI)
Crystal data	
Chemical formula	$C_{25}H_{32}O_3$
Chemical formula weight	380.53
Cell setting	Triclinic
Space group	$P\overline{1}$
a (Å)	10.830 (2)
b (Å)	12.717 (2)
c (Å)	9.379 (1)
α (°)	104.53 (1)
β (°)	99.15 (1)
γ (°)	105.14 (1)
V (Å^3)	1171.6 (3)
Z	2
D_x (Mg m^{-3})	1.079
Radiation type	Mo $K\alpha$
Wavelength (Å)	0.71073
No. of reflections for cell parameters	25
θ range (°)	10–15
μ (mm^{-1})	0.069
Temperature (K)	293
Crystal form	Prism
Crystal size (mm)	0.5 × 0.4 × 0.4
Crystal colour	Colourless
Data collection	
Diffractometer	Rigaku AFC-5
Data collection method	θ–2θ scans
Absorption correction	None
No. of measured reflections	4353
No. of independent reflections	4115
No. of observed reflections	2456
Criterion for observed reflections	$\|F_o\| > 3\sigma(\|F_o\|)$
$R_{\rm int}$	0.013
$\theta_{\max}$ (°)	25

	(XI)
Range of h, k, l	$0 \rightarrow h \rightarrow 12$ $-15 \rightarrow k \rightarrow 15$ $-11 \rightarrow l \rightarrow 11$
No. of standard reflections	3
Frequency of standard reflections	Every 100 reflections
Intensity decay (%)	4
Refinement	
Refinement on	F
R	0.068
wR	0.072
S	1.16
No. of reflections used in refinement	2456
No. of parameters used	253
H-atom treatment	H atoms riding
Weighting scheme	$w = 1/[\sigma^2(F) + 0.0009F^2]$
$(\Delta/\sigma)_{\max}$	0.004
$\Delta\rho_{\max}$ (e Å^{-3})	0.24
$\Delta\rho_{\min}$ (e Å^{-3})	−0.28
Extinction method	None
Source of atomic scattering factors	*International Tables for X-ray Crystallography* (1974, Vol. IV)
Computer programs	
Data collection	*MSC/AFC* (Molecular Structure Corporation, 1988)
Cell refinement	*MSC/AFC*
Data reduction	Local programs
Structure solution	*CRYSTAN-GM* (Edwards *et al.*, 1995)
Structure refinement	*CRYSTAN-GM*
Preparation of material for publication	*CRYSTAN-GM*

Table 3. *Selected geometric parameters (Å, °) for (X)*

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 $U_{\rm eq}$ 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 carbonyl plane is almost perpendicular to the triisopropylphenyl ring, the dihedral angle φ_A being 79 (1)–89 (1)° (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 *ortho*-isopropyl groups along with the angle φ_A. The greater the deviation of φ_A from 90°, the shorter one of the O···C(isopropyl) distances becomes, which seems favourable for hydrogen abstraction by the excited carbonyl O atom in photoirradiation. Indeed, (II), (VI) and (VII) have φ_A = 79 (1)–82 (1)° 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 CH$_3$—C—CH$_3$ bond angles. The shorter the C—CH$_3$ bond distances, which are artefact owing to the disorder, the larger the CH$_3$—C—CH$_3$ bond angle. In the photostable crystals (IX) and (X) there is a small degree of disorder, indicating a good efficiency of molecular packing.

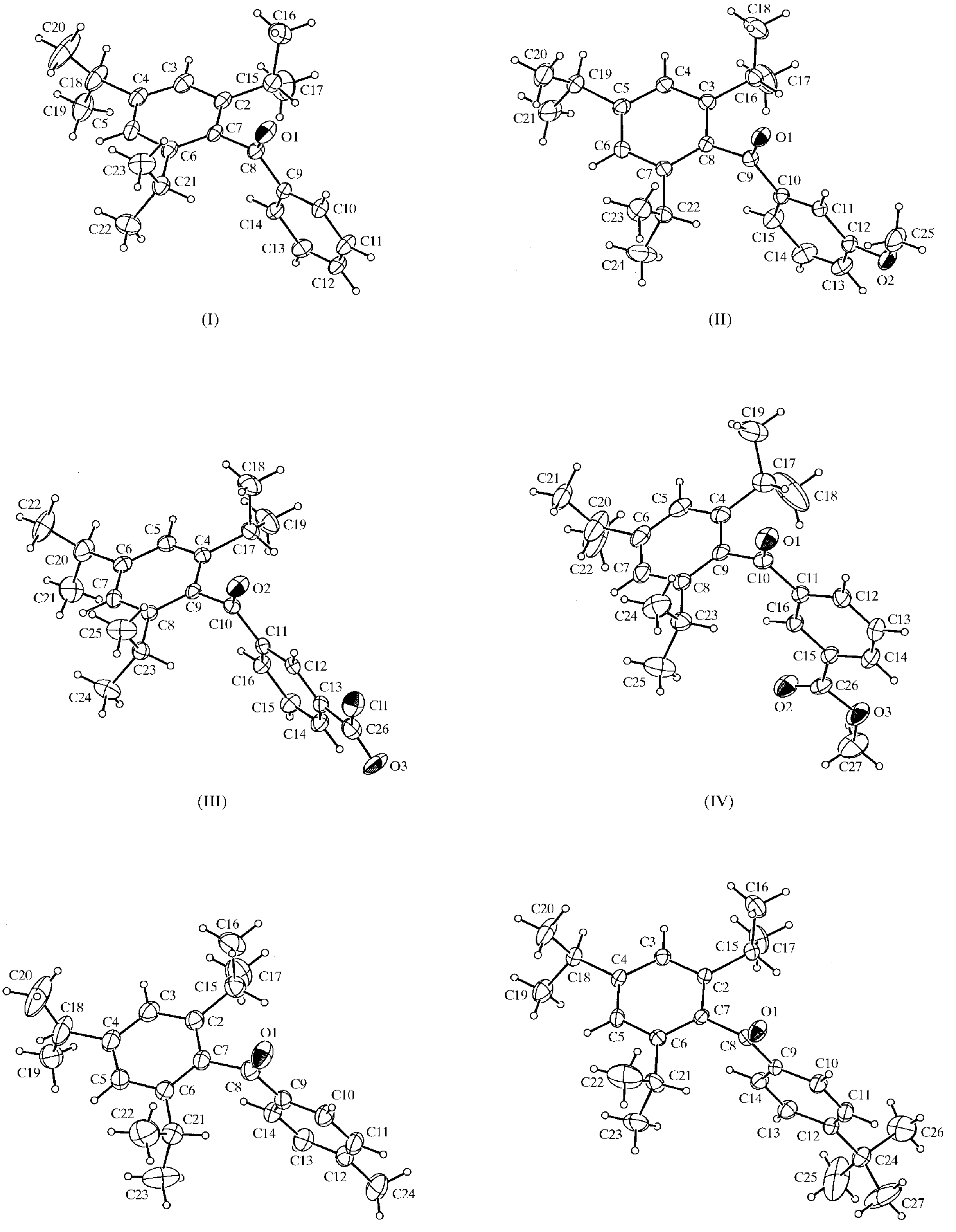
Table 4. *Dihedral angles (°) between the carbonyl O═C< plane and phenyl rings A and B*

A is the triisopropylphenyl group and *B* the 3′- or 4′-substituted phenyl group. The standard uncertainties of the dihedral angles are ~1°.

	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

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

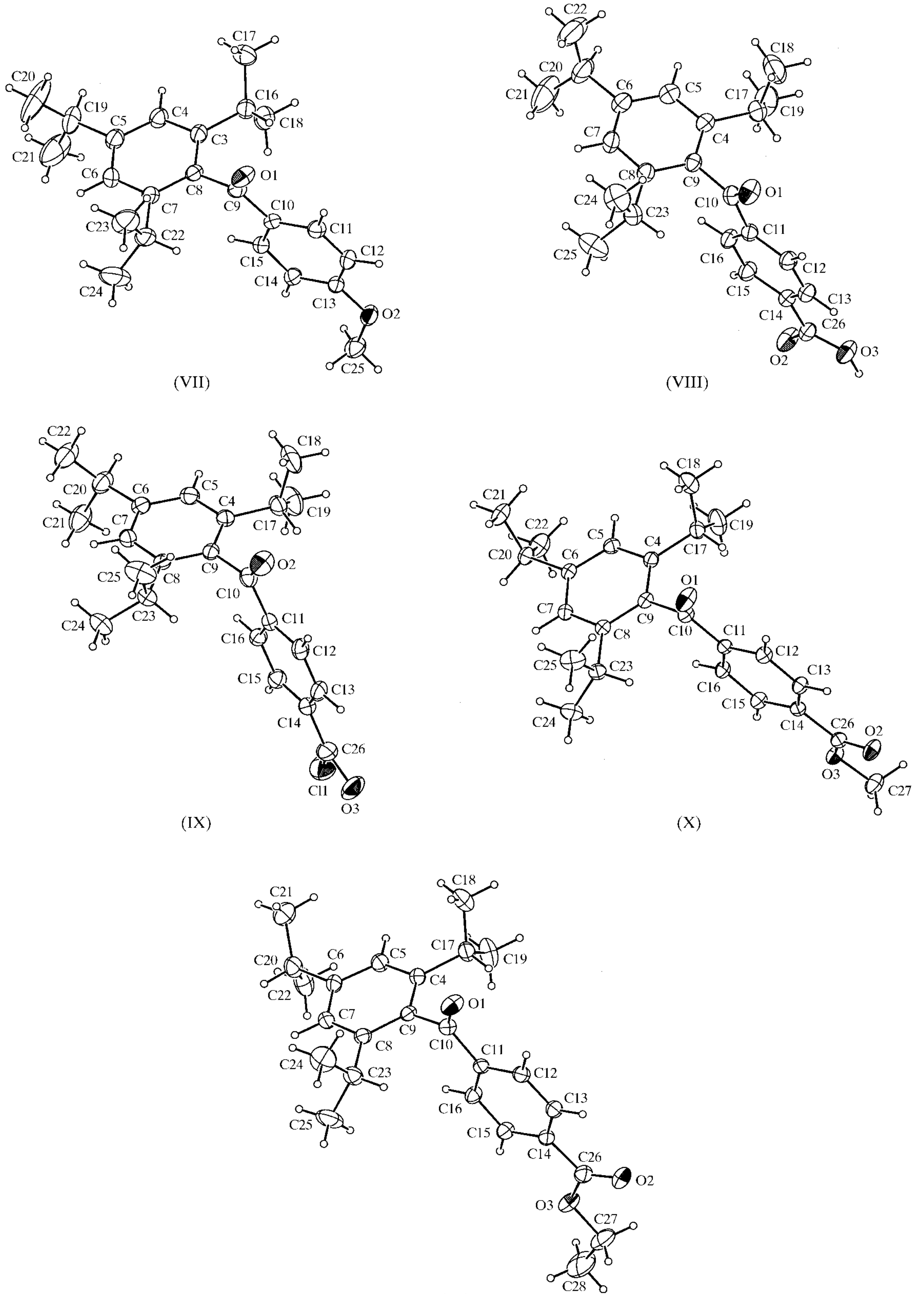


(I) (II)

(III) (IV)

(V) (VI)

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.



(VII) (VIII)

(IX) (X)

(XI)

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), 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

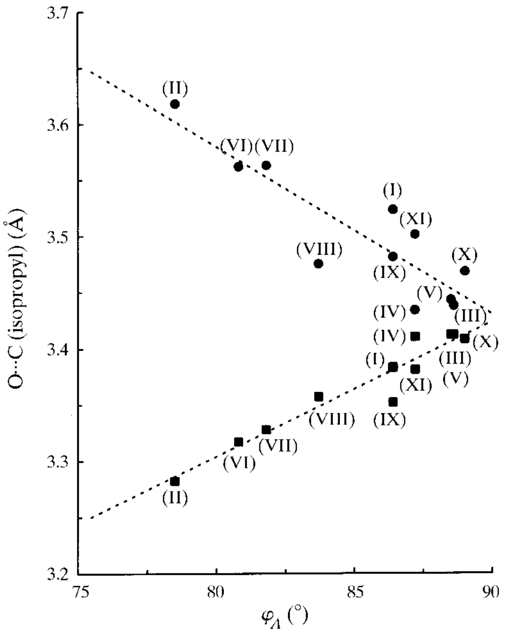


Fig. 2. Correlation between the dihedral angle (φ_A) in Table 4 and the intramolecular O(carbonyl)···C(isopropyl central) distances. The broken lines are the regression lines for longer and shorter O···C distances.

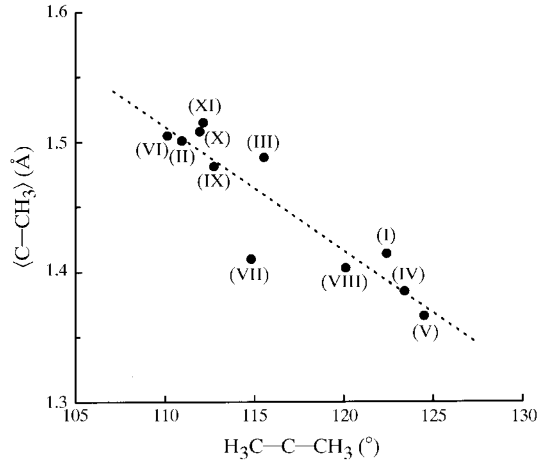
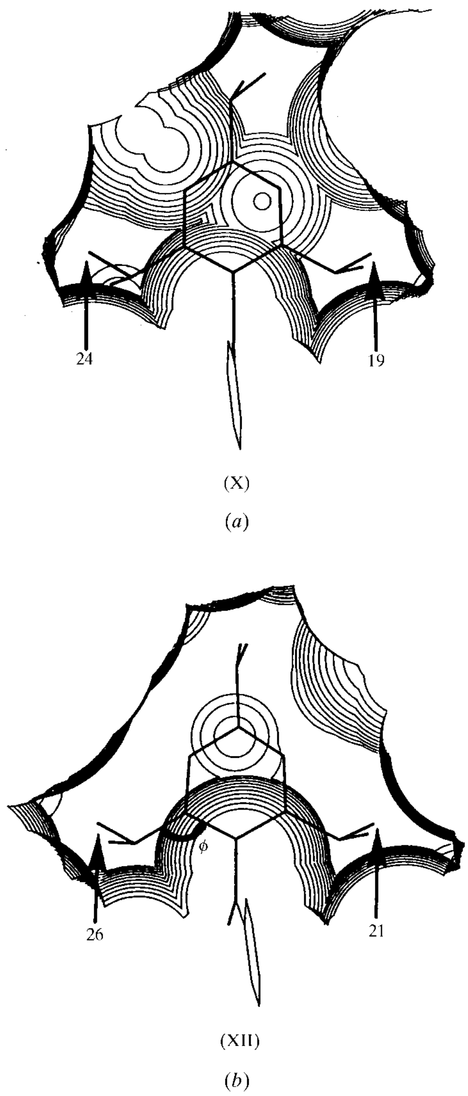


Fig. 3. Correlation between the CH_3-C-CH_3 bond angle and the average of the $C-CH_3$ bond distances for the isopropyl group at position 4. The broken line is the regression line.



(X)
(*a*)

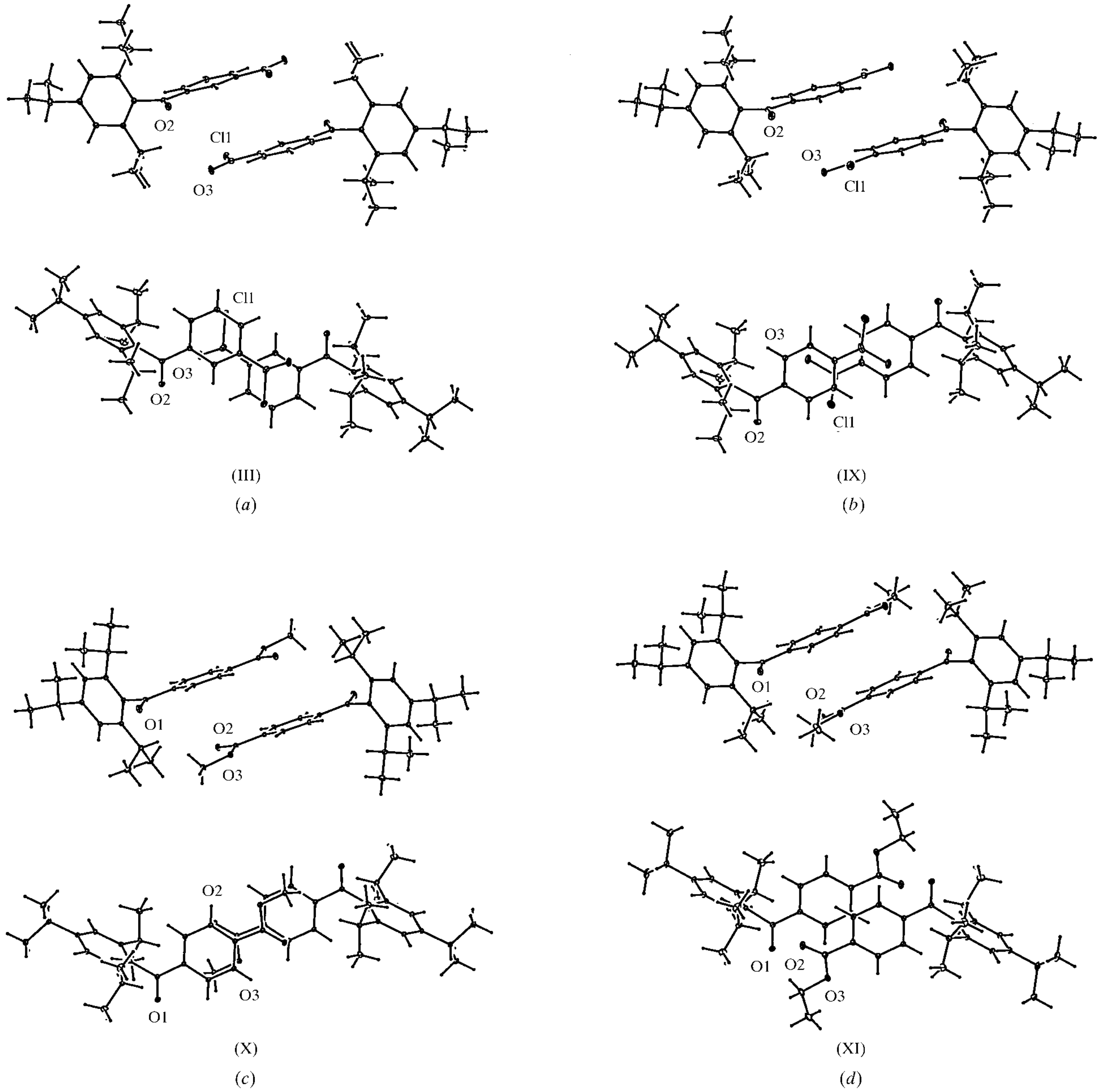
(XII)
(*b*)

Fig. 4. Sections of the reaction cavity of the triisopropylphenylcarbonyl moiety in (*a*) (X) and (*b*) (XII) parallel to the phenyl plane, with a shift downward from the plane at 0.5–1.5 Å. The carbonyl O atom is located upward from the plane.

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



(III)
(*a*)

(IX)
(*b*)

(X)
(*c*)

(XI)
(*d*)

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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