

***Darzens* Reaction as a Convenient Method for the Synthesis of α -Chloroketones, α -Chloroepoxides, and Symmetrically Substituted Dioxines**

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Summary. The *Darzens* reaction of dichloroacetophenone (*DCAP*) with substituted benzaldehydes has been studied. The structure of the products was shown to depend on the phenyl group substituents. Reaction of benzaldehyde, 4-bromo-, and 2,4-dichlorobenzaldehydes results in 1-phenyl-3-aryl-3-chloropropane-1,2-diones (**2a–c**), reaction of *para*- or *meta*-nitrobenzaldehydes yields 1-phenyl-2-chloro-3-aryl-2,3-epoxypropane-1-ones (**3a, b**). Upon the introduction of an alkoxy group into the phenyl ring of benzaldehyde and/or dichloroacetophenone, symmetrically substituted dioxines were obtained (**6a–c**). The structure of the reaction products has been established by single crystal X-ray investigations.

Keywords. *Darzens* reaction; α -Chloroketone; α -Chloroepoxide; Substituted dioxine; Molecular structure; Crystal structure.

***Darzens*-Reaktion als bequemes Verfahren zur Synthese von α -Chloroketonen, α -Chloroepoxiden und symmetrisch substituierten Dioxinen**

Zusammenfassung. Die *Darzens*-Reaktion von Dichloracetophenon (*DCAP*) mit substituierten Benzaldehyden wurde untersucht. Die Struktur der Produkte ist von den Substituenten an der Phenylgruppe abhängig. Die Umsetzung mit Benzaldehyd, 4-Brom- und 2,4-Dichlorbenzaldehyd liefert 1-Phenyl-3-aryl-3-chloropropan-1,2-dione (**2a–c**), die Reaktion von *para*- oder *meta*-Nitrobenzaldehyd 1-Phenyl-2-chloro-3-aryl-2,3-epoxypropan-1-one (**3a, b**). Durch Einführung einer Alkoxygruppe in den Phenylring des Benzaldehyds und/oder des Dichloracetophenons erhält man symmetrisch substituierte Dioxine (**6a–c**). Die Struktur der Reaktionsprodukte wurde mittels Röntgenstrukturanalyse bestätigt.

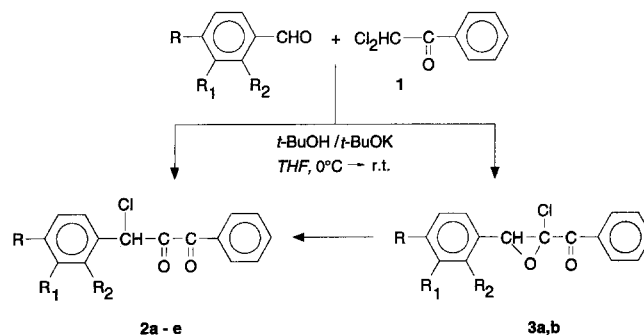
Introduction

The condensation of aldehydes and ketones with α -halo esters in the presence of bases, leading to the formation of α,β -epoxyesters, is known as *Darzens* reaction [1]. Earlier, we have reported on the interaction of amides [2] and methyl esters of dichloroacetic acid [3] and dichloro-*tert*-butylketone [4] with substituted benzalde-

hydes *via Darzens* type condensations. Amides were shown to form the amides of 3-phenyl-3-chloro-2-oxopropionic acid by reaction with benzaldehydes. In the case of dichloroacetic acid methyl ester, there were obtained esters of both 3-aryl-3-chloro-2-oxopropionic acid and 2-chloro-3-aryl-2,3-epoxypropionic acid or a mixture of these products, depending on the substituents in the aldehyde molecule. In the case of dichloromethyl-*tert*-butylketone, 1-aryl-1-chloro-4,4-dimethylpentane-2,3-diones and 1-aryl-1-chloro-1,2-epoxy-4,4-dimethylpentanones were formed, the α -chloro-epoxides being transformed into α -chloroketones when left to stand at room temperature. A. Takeda and coworkers [5] studied the reaction of aliphatic aldehydes with esters of dichloroacetic acid; it was shown that, depending on the number of carbon atoms in the aldehyde molecule, α -chloroketones and α -chloro-epoxydes could be obtained. They also investigated the thermic isomerization of α -chloro-epoxides to α -chloroketones. The *Darzens* reaction products have been successfully used as intermediates in the synthesis of thiazoles [6], oxazoles [7], oxathiines and dithiines [8], imidazopyridines [9], quinoxalines [10] and in the asymmetric synthesis of 2,3-epoxy compounds [5]. The present paper deals with reactions of dichloroacetophenone (**1**, *DCAP*), with benzaldehydes.

Results and Discussion

The condensation of *DCAP* with benzaldehyde and 4-bromo- and 2,4-dichloro-benzaldehydes in *tert*-BuOH in the presence of *tert*-BuOK proceeds with formation of 1-phenyl-3-aryl-3-chloropropane-1,2-diones **2a–c** in good yields.



	2a	2b	2c	2d	2e	3a	3b
R	H	Br	Cl	NO ₂	H	NO ₂	H
R ¹	H	H	H	H	NO ₂	H	NO ₂
R ²	H	H	Cl	H	H	H	H

Reaction of *DCAP* with nitrobenzaldehydes leads to 1-phenyl-2-chloro-3-aryl-2,3-epoxypropane-1-ones **3a, b**. The latter, when left to stand at room temperature for a long time (7 weeks) or heated to reflux in benzene, are transformed to the corresponding compounds **2a, b** which is indicated by a shift of the singlets of the epoxide protons in the ¹H NMR spectrum from ~4.50 to ~6.30 ppm for **3** and **2**,

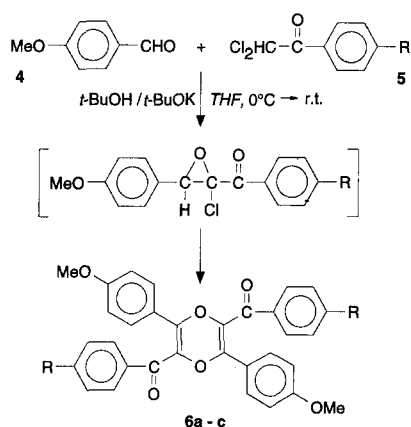
Table 1. Physical parameters and spectral data for compounds **2** and **3**

Compound	b.p. (°C/mm) or m.p. (°C)	Molecular formula ^a	IR (film) ν (cm ⁻¹)	¹ H NMR δ (ppm)
2a^b	148–150/0.03 39–40	C ₁₆ H ₁₁ ClO ₂ (258.6)	1730, 1675, 1600, 1530, 1500, 1450, 1320, 1295, 1185, 1100, 1080, 1035, 740, 720, 710	CCl ₄ ; 6.23 (s, 1H, CHCl); 7.00–8.00 (m, 10H, 2C ₆ H ₅)
2b	170–173/0.03 50	C ₁₆ H ₁₀ BrClO ₂ (337.5)	1725, 1680, 1590, 1450, 1320, 1300, 1290, 1180, 1110, 1080, 1020, 920	(CD ₃) ₂ SO; 6.30, (s, 1H, CHCl); 7.00–8.10 (m, 9H, C ₆ H ₅ , C ₆ H ₄ Br)
2c	158–160/0.03	C ₁₆ H ₉ Cl ₃ O ₂ (327.5)	1730, 1680, 1590, 1475, 1450, 1390, 1285, 1110, 1055, 880, 805, 750, 710	CD ₃ CN; 6.80 (s, 1H, CHCl); 7.00–8.10 (m, 8H, C ₆ H ₅ , C ₆ H ₃ Cl ₂)
2d	95–96°	C ₁₆ H ₁₀ ClNO ₄ (303.6)	1725, 1670, 1600, 1525, 1460, 1450, 1350, 1275, 1200, 840, 780, 740	CCl ₄ ; 6.23 (s, 1H, CHCl); 7.20–8.33 (m, 9H, C ₆ H ₅ , C ₆ H ₄ -NO ₂ - <i>p</i>)
2e	89–90°	C ₁₆ H ₁₀ ClNO ₄ (303.6)	3080, 1725, 1675, 1595, 1530, 1450, 1360, 1270, 1110, 885, 770, 735	CD ₃ CN; 6.43 (s, 1H, CHCl); 7.02–8.03 (m, 9H, C ₆ H ₅ , C ₆ H ₄ NO ₂ - <i>m</i>)
3a	102–103	C ₁₆ H ₁₀ ClNO ₂ (303.6)	1695, 1595, 1540, 1485, 1460, 1355, 1260, 1125, 965, 915, 875, 840, 815	CD ₂ Cl ₂ ; 4.50 (s, 1H, CH); 7.20–8.23 (m, 9H, C ₆ H ₅ , C ₆ H ₄ NO ₂ - <i>p</i>)
3b	116–117	C ₁₆ H ₁₀ ClNO ₄ (303.6)	3095, 1690, 1600, 1530, 1455, 1360, 1350, 1250, 1125, 970, 870, 840, 810	CDCl ₃ ; 4.55 (s, 1H, CH); 7.16–8.40 (m, 9H, C ₆ H ₅ , C ₆ H ₄ NO ₂ - <i>m</i>)

^a Satisfactory microanalyses were obtained for all compounds. ^b Makosza M., Kwast A., Kwast E., *J. Org. Chem.* **50**, 3722 (1985) δ = 6.20, (s, 1H, CHCl); 7.0–8.0 (m, 10H, 2C₆H₅). ^c Compounds **2d**, **e** were recrystallized from hexane

respectively. Physical constants and spectral data for compounds **2a–e** and **3a**, **b** are shown in Table 1.

In our papers published so far, we have established that the introduction of an alkoxy group into the *para* position of benzaldehydes and *DCAP* leads to symmetrically substituted dioxines, which are likely to be the result of a dimerization of the product of the first stage of the *Darzens* reaction.



6	R	Yield, %
a	H	38
b	OMe	36
c	OEt	40

Physical constants and spectral data of compounds **6a-c** are listed in Table 2. The quality of the ^1H NMR spectrum of compound **6b** is not satisfactory due to its poor solubility. Thus, it was additionally identified by mass spectrometry (see Experimental) and X-ray analysis (Fig. 1).

The dioxine ring of **6a** is planar. The distribution of bond lengths in the heterocycle indicates the absence of conjugation: the $\text{C}^2=\text{C}^3$ double bond ($1.327(5) \text{ \AA}$) has the same length as that in cyclohexene ($1.327(12) \text{ \AA}$) [11]. As to C–O bonds (average $1.394(4) \text{ \AA}$), they are somewhat longer than those in furan rings (average $1.368(15) \text{ \AA}$) [11]. The geometry of the substituents in **6a** shows no anomalies.

Table 2. Physical parameters and spectral data for dioxines **6**

Compound	m.p.	Molecular formula	IR (film) ν (cm^{-1})	^1H NMR CDCl_3 , δ (ppm)
a	194.5–195.5	$\text{C}_{32}\text{H}_{24}\text{O}_6$	1675, 1610, 1579, 1515, 1465, 1450, 1260, 1180, 1170	3.63 (s, 6H, 2CH_3); 6.31–7.87 (m, 18H, $2\text{C}_6\text{H}_4$, $2\text{C}_6\text{H}_5$)
b	220–221	$\text{C}_{34}\text{H}_{28}\text{O}_8$	1670, 1630, 1605, 1575, 1515, 1465, 1355, 1285, 1260, 1180, 1170, 1025	
c	208–210	$\text{C}_{36}\text{H}_{32}\text{O}_8$	1680, 1540, 1605, 1580, 1515, 1470, 1360, 1270, 1260, 1170, 1030, 915	1.38 (t, 3H, $\text{CH}_3\text{CH}_2\text{O}$); 3.63 (q, 2H, $\text{CH}_3\text{CH}_2\text{O}$); $\delta_{\text{A}} = 8.27$, $\delta_{\text{B}} = 6.12$, $J_{\text{AB}} = 9 \text{ Hz}$; $\delta_{\text{C}} = 7.43$, $\delta_{\text{D}} = 6.23$, $J_{\text{CD}} = 9 \text{ Hz}$

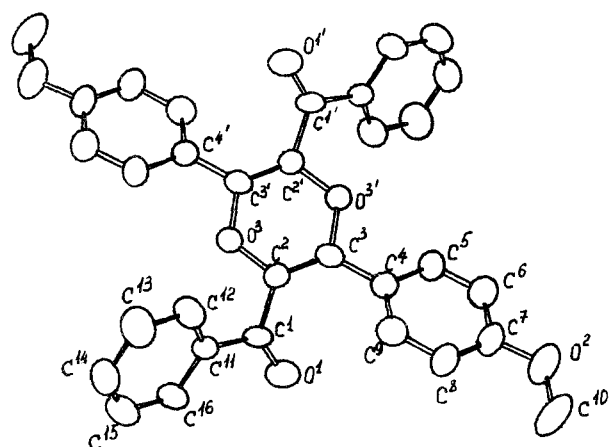
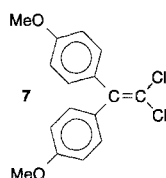


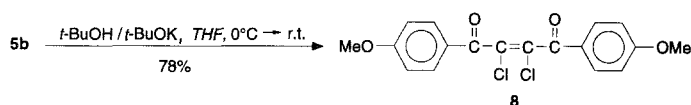
Fig. 1. Atom numbering scheme for structure **6a**

Methods for the synthesis of 1,4-dioxines *via* dehydrohalogenation of *trans*-2,3-dichloro-1,4-dioxane and isomers of 2,3,5,6-tetrachloro-1,4-dioxane using MgI_2 in the presence of metallic Mg are known [12]. These methods include many steps and are rather laborious while the synthesis of dioxines according to *Darzens* is experimentally easy and economical, starting from readily available precursors. 1,1-Bis-(4'-methoxyphenyl)-2,2-dichloroethene (**7**) has been isolated from the reaction mixture as a result of the condensation of anisaldehyde (**4**) and 4-methoxy-dichloroacetophenone (**5**) with a yield of 3% [13].



The structure of compound **7** has been determined by X-ray analysis. The molecule has C_2 symmetry, the C_2 axis coinciding with the $\text{C}=\text{C}$ double bond (Fig. 2). Its bond length is close to that of tetrasubstituted ethenes (average 1.331(9) Å) [11] and the $\text{C}-\text{Cl}$ bond, 1.730(1) Å, is nearly the same as in 1,1-dichloroethenes (average 1.720(13) Å) [11]. The $\text{C}=\text{C}$ double bond in **7** is slightly distorted (torsional angle $\text{Cl}-\text{C}^1=\text{C}^2-\text{C}^3$: 9.5°). The plane of the aryl substituents is twisted by about 48° relative to the ethene fragment, excluding conjugation between these fragments.

It could be supposed that **7** is a product of self-condensation of **5b** under the conditions of the *Darzens* reaction. However, it could be shown that self condensation **5b** results in 1,2-bis-(4'-methoxybenzoyl)-1,2-dichloroethene (**8**).



An X-ray study of **8** showed its C_2 symmetry, the twofold axis lying in the plane of the ethene fragment perpendicular to the $\text{C}=\text{C}$ bond and intersecting it in the middle (Fig. 3). The length of the double bond (1.329(7) Å) is the same as in **7** within experimental errors.

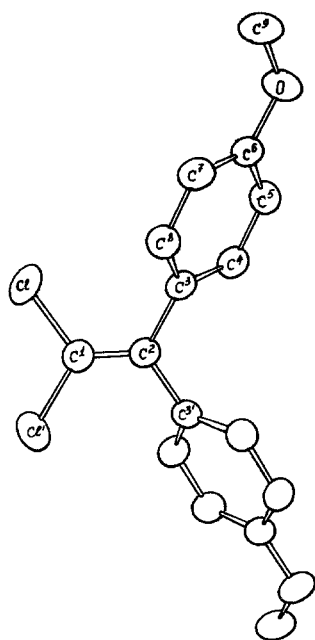


Fig. 2. Atom numbering scheme for structure 7

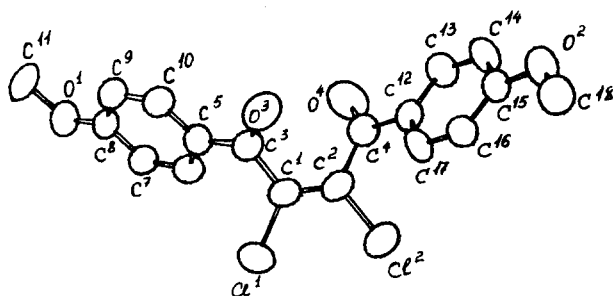


Fig. 3. Atom numbering scheme for structure 8

The methoxybenzoyl fragments in **8** are not planar: the distances of O³ and O⁴ from the planes of the corresponding benzene rings are equal to $-0.335(5)$ and $0.258(6)$ Å. The planes of the carbonyl groups at C³ and C⁴ constitute dihedral angles of 52° and 61° with the plane of ethene fragment, excluding conjugation.

Experimental

¹H NMR spectra were recorded on a Varian T-60 (60 MHz) spectrometer. IR-spectra were obtained using a UR-20 spectrometer. High-resolution EI mass spectra were recorded on a MX-1310 instrument (ionizing voltage: 70 V, ionizing current: 30 mA, temperature of ion source: 120 °C).

3-Chloro-1,3-diphenylpropane-1,2-dione (**2a**)

A solution of *t*-BuOK in *t*-BuOH, obtained by reaction of 3.0 g (0.077 g atom) K with 50 ml *t*-BuOH, was added to a stirred mixture of 8.1 g (77 mmol) benzaldehyde and 14.5 g (77 mmol) DCAP in 20 ml of THF in an argon atmosphere at 0–5 °C. The mixture was left for 40 h at r.t. The solvent was removed *in vacuo* by rotatory evaporation. Brine was added to the residue and the mixture was extracted with

chloroform (3 \times 80 ml). The extract was dried with MgSO₄ and chloroform was removed. After distilling, compound **2a** was obtained; yield: 15.4 g (77%) (Table 1).

Compounds **2b** and **2c** were obtained following the above method using the corresponding benzaldehyde and DCAP. In case of 4- and 3-nitrobenzaldehydes, diethyl ether was added to the mixture after removing the chloroform. Products **2d** and **2e** crystallize on standing at r.t. Physical properties and spectral data are given in Table 1.

Isomerization of α -chloroepoxides **3a, b** to α -chloroketones **2d, e**

A solution of 0.05 mol of α -chloroepoxide **3a, b** in 20 ml of benzene was refluxed until the singlet at 4.50 ppm in the ¹H NMR spectrum disappeared (3h). Benzene was removed *in vacuo* and the residue was recrystallized from hexane.

2,5-Dibenzoyl-3,4-bis-(4'-methoxyphenyl)-dioxine (**6a**)

A solution of *t*-BuOH was added to a stirred mixture of equimolar quantities of anisaldehyde and DCAP in THF in an argon atmosphere at 0–5 °C. The mixture was kept at ~20 °C for 48 h. The solvent was removed *in vacuo* by rotary evaporation. The residue was treated with brine and extracted with chloroform. The extract was dried with MgSO₄. After removing chloroform, the crystals of **6a** were washed with ether. Compound **6c** was obtained similar to **6a**.

In case of the reaction of anisaldehyde with 4-methoxy-dichloroacetophenone, a part of reaction mixture was insoluble in chloroform. It was filtered, dried with air and recrystallized from dimethylformamide yielding compound **6b** was obtained (Table 2). The mass spectrum of compound **6b** contains a molecular ion peak at $m/z = 564$ with a relative intensity of 8%, corresponding to an elemental composition of C₃₄H₂₈O₈; calculated ion mass: 564.1784, experimental ion mass: 564.1779. Mass spectrum of **6b** (m/z , ($I/I_{\max} \times 100$), [elemental composition of ion]): 565 (3) [C₁¹³C₃₃H₂₈O₈ + DC₃₄H₂₇O₈]; 564 (8) [C₃₄H₂₈O₈]; 430 (1) [C₂₆H₂₂O₆]; 429 (2) [C₂₆H₂₁O₆]; 266 (1) [C₁₇H₁₄O₃]; 159 (2) [C₁₀H₇O₂]; 136 (10) [C₁¹³C₇H₇O₂ + DC₈H₆O₂]; 135 (100) [C₈H₇O₂]; 107 (4) [C₇H₇O]; 92 (4) [C₆H₄O].

After evaporation of chloroform from the extract, the residue was recrystallized from *i*-PrOH, yielding compound **7**: m.p. 111 °C (113 °C in [13]); IR (nujol): $\nu = 1605, 1515, 1305, 1255, 1180, 1040, 840 \text{ cm}^{-1}$; ¹H NMR ((CD₃)₂CO, TMS): $\delta = 3.73 \text{ ppm}$ (s, 6H, 2CH₃O), phenyl protons observed as AB system ($\delta_A = 7.11 \text{ ppm}$, $\delta_B = 6.72 \text{ ppm}$, $J_{AB} = 9.5 \text{ Hz}$).

1,2-Bis-(4'-methoxybenzoyl)-1,2-dichloroethene (**8**)

A solution of *t*-BuOK in *t*-BuOH, obtained by reaction of 0.78 g (0.02 g atom) K with 15 ml of *t*-BuOH, was added to the stirred solution of 4.4 g (0.02 mol) 4-methoxy-dichloroacetophenone in 10 ml of THF in an argon atmosphere at 0–5 °C. The mixture was kept at ~20 °C for 24 h. After the usual procedure given above, compound **8** was recrystallized from *i*-PrOH. Yield: 3.2 g (78%), m.p. 131–132 °C; IR (nujol): $\nu = 1670, 1655, 1600, 1575, 1460, 1260, 1180, 855 \text{ cm}^{-1}$; ¹H NMR ((CD₃)₂CO, TMS): $\delta = 3.50 \text{ ppm}$ (s, 6H, 2CH₃O), phenyl protons observed as AB system: $\delta_A = 7.61 \text{ ppm}$, $\delta_B = 6.65 \text{ ppm}$, $J_{AB} = 9 \text{ Hz}$.

X-ray Structure Determination of **6a, 7, and 8**

A summary of the structure determination parameters is given in Table 3. Lists of structure factors, atomic coordinates, and anisotropic thermal parameters have been deposited at the Fachinformationszentrum Karlsruhe and are available from one of us (I.A.L.).

Table 3. Structure determination parameters for compounds **6a**, **7**, and **8** at 20 °C

	6a	7	8
Empirical formula	C ₃₂ H ₂₂ O ₆	C ₁₆ H ₁₄ O ₂ Cl ₂	C ₁₈ H ₁₄ O ₄ Cl ₂
Color, habit	Red prisms	Colorless slides	Colorless slides
Crystal size (mm)	0.4 × 0.2 × 0.2	0.4 × 0.3 × 0.05	0.3 × 0.2 × 0.05
Crystal system	monoclinic	monoclinic	monoclinic
Space group	P2 ₁ /n	C2/c	P2 ₁ /n
Unit cell dimensions (from 25 high angle reflections)	<i>a</i> = 4.648(2) Å <i>b</i> = 12.828(3) Å <i>c</i> = 21.370(5) Å <i>β</i> = 95.77(3)°	18.275(7) Å 7.964(3) Å 11.098(8) Å 115.80(4)°	8.928(2) Å 9.540(3) Å 20.136(7) Å 93.52(2)°
Volume, (Å ³)	1268(1)	1454(2)	1712(1)
<i>Z</i>	2	4	4
Formula weight	504.54	309.19	365.22
Density (calc g·cm ⁻³)	1.32	1.41	1.42
Absorption coefficient (cm ⁻¹)	0.851	4.431	3.957
F(000)	528	640	752
Diffractometer used	Enraf Nonius CAD-4		
Radiation	MoK _α (λ = 0.71073 Å), graphite monochromator		
2θ range (deg.)	4–50	4–54	4–52
Scan mode	ω/(2θ)	ω/(5/3θ)	ω/(2θ)
Scan speed	Variable; 2°–20° min ⁻¹ in σ(I)		
Standard reflections	Two intensity and two orientation control reflections measured every 200 reflections		
Index range	–6 ≤ <i>h</i> ≤ 6, 0 ≤ <i>k</i> ≤ 14, 0 ≤ <i>l</i> ≤ 23	–21 ≤ <i>h</i> ≤ 19, 0 ≤ <i>k</i> ≤ 9, 0 ≤ <i>l</i> ≤ 12	–10 ≤ <i>h</i> ≤ 10, 0 ≤ <i>k</i> ≤ 11, 0 ≤ <i>l</i> ≤ 21
Reflections collected	2010	1350	2290
Observed reflections	858	1040	1194
System	SDP-PLUS, PDP-11/23		
Solution	Direct methods		
Refinement method	Full-matrix least squares (on <i>F</i> 's)		
Quantity minimized	Σω(<i>F</i> _o – <i>F</i> _c) ²		
Hydrogen atoms	From difference Fourier method		
	not refined	refined	not refined
	fixed <i>B</i> (iso) = 4 Å ²	isotropically	fixed <i>B</i> (iso) = 4 Å ²
Weighting scheme	ω = (4 <i>F</i> _o ² /(σ(<i>I</i>)) ² + (0.07· <i>F</i> _o ²) ²)		
Final <i>R</i> indices (observed data)	<i>R</i> = 0.052 <i>R</i> _w = 0.070	<i>R</i> = 0.029 <i>R</i> _w = 0.048	<i>R</i> = 0.052 <i>R</i> _w = 0.079
Goodness of fit	1.716	1.239	1.896
Largest Δ/δ	0.01	0.45	0.16
Data to parameter ratio	4.98	8.67	5.50
Largest difference peak (A ⁻³)	0.25	0.30	0.28

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