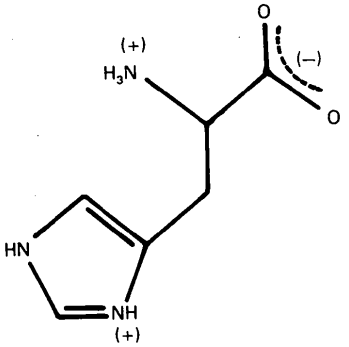

Fig. 2. Electronic situation of the L-histidine group in the title compound.

H(3N1) has difficulties in finding an acceptor which is properly located. This situation is not uncommon, mainly when a hydrogen-rich group like NH_3^+ belongs to a large organic group (Olovsson & Jönsson, 1976).

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(5*RS*)-3,4-Dichloro-5-dichloromethyl-5-acetoxy-2(5*H*)-furanone

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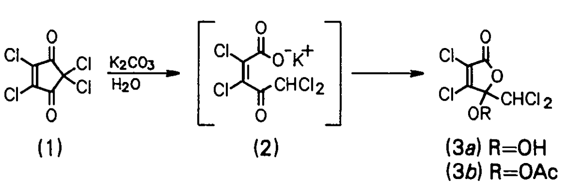
Abstract. 3,4-Dichloro-5-dichloromethyl-2(5*H*)-oxo-5-furyl acetate, $C_7H_4Cl_4O_4$, $M_r = 293{\cdot}92$, monoclinic, $P2_1/n$, $a = 16{\cdot}139$ (1), $b = 8{\cdot}9486$ (5), $c = 15{\cdot}994$ (1) Å, $\beta = 96{\cdot}669$ (8)°, $V = 2294{\cdot}2$ (3) Å^3, $Z = 8$, $D_x = 1{\cdot}702$ g cm^{-3}, Cu $K\alpha$, $\lambda_{\alpha_1} = 1{\cdot}540562$ Å, $\mu = 95{\cdot}8$ cm^{-1}, $F(000) = 1168$, 295 K, $R = 0{\cdot}062$ ($wR = 0{\cdot}067$) for 2689 unique reflections with $I \geq 2\sigma(I)$. The asymmetric unit contains two virtually identical molecules having normal geometry. Molecules are linked by possible weak C—H···O hydrogen bonds, C···O = 3·311 (9) and 3·23 (1) Å.

Introduction. Treatment of 2,2,4,5-tetrachlorocyclopentene-1,3-dione (1), a constituent of pulp mill bleach liquors (McKague, de Sousa, Strömberg & Kringstad, 1987), with potassium carbonate and acetic anhydride gives a crystalline acetate which is identical to a compound which appears during the analysis of chlorophenols in the liquors (Strömberg, de Sousa, Ljungquist, McKague & Kringstad, 1987). Thus, a simple method was available by which material could be prepared for identification much more easily than by isolation from the liquor. This paper describes the X-ray structure of the acetate; other spectral data have been published separately (Strömberg *et al.*, 1987).



Experimental. Colorless crystals, 0·25 × 0·32 × 0·35 mm, faces {10$\bar{1}$}, {110}, {011}, {100}. Enraf–Nonius CAD-4F diffractometer, lattice parameters from 25 reflections with $\theta = 25$–41°, intensities for $\theta \leq 75°$, *hkl*: 0 to 20, 0 to 11, −20 to 20, ω–2θ scan, ω scan width $(0{\cdot}75 + 0{\cdot}14\tan\theta)°$ at 1·1–10·0° min^{-1}, extended 25% on each side for background measure-

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Table 1. *Final positional (fractional* × 10^4) *and equivalent isotropic thermal parameters* ($U \times 10^3$ Å^2) *with e.s.d.'s in parentheses*

$$U_{eq} = \tfrac{1}{3}\textstyle\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Cl(1)	3560 (2)	2270 (3)	5095 (1)	67
Cl(2)	5075 (1)	891 (3)	3933 (2)	72
Cl(3)	3502 (2)	2166 (3)	2143 (1)	65
Cl(4)	3232 (2)	−765 (3)	1415 (2)	78
O(1)	2769 (3)	−275 (6)	3190 (3)	39
O(2)	1983 (3)	668 (6)	4125 (4)	55
O(3)	3913 (3)	−1819 (6)	3088 (4)	50
O(4)	3543 (4)	−2290 (7)	4388 (4)	65
C(1)	2648 (4)	546 (9)	3896 (5)	36
C(2)	3461 (5)	1145 (9)	4242 (5)	39
C(3)	4036 (4)	619 (9)	3820 (5)	39
C(4)	3630 (4)	−331 (8)	3091 (5)	36
C(5)	3834 (5)	−2729 (10)	3785 (6)	55
C(6)	4146 (7)	−4236 (11)	3615 (7)	79
C(7)	3795 (5)	267 (9)	2227 (5)	45
Cl(1′)	10117 (1)	1048 (3)	3619 (2)	67
Cl(2′)	9025 (2)	2569 (3)	5139 (1)	83
Cl(3′)	7177 (1)	1080 (3)	3633 (2)	69
Cl(4′)	6439 (1)	4006 (3)	3377 (2)	86
O(1′)	8168 (3)	3447 (6)	2805 (3)	40
O(2′)	9051 (4)	2372 (7)	1996 (3)	61
O(3′)	8108 (3)	5110 (6)	3911 (3)	48
O(4′)	9376 (3)	5548 (6)	3508 (4)	60
C(1′)	8849 (4)	2599 (9)	2671 (5)	38
C(2′)	9254 (4)	2106 (9)	3506 (5)	38
C(3′)	8835 (4)	2690 (9)	4078 (5)	41
C(4′)	8110 (5)	3599 (9)	3685 (5)	39
C(5′)	8769 (5)	6001 (9)	3775 (5)	45
C(6′)	8600 (6)	7558 (10)	4020 (7)	68
C(7′)	7275 (5)	2970 (9)	3903 (6)	48

Table 2. *Bond lengths* (Å), *bond angles* (°) *and intra-annular torsion angles* (°) *with e.s.d.'s in parentheses*

Cl(1)–C(2)	1·688 (8)	1·676 (7)	O(3)–C(5)	1·397 (10)	1·370 (9)
Cl(2)–C(3)	1·684 (7)	1·692 (8)	O(4)–C(5)	1·188 (10)	1·184 (9)
Cl(3)–C(7)	1·765 (8)	1·748 (8)	C(1)–C(2)	1·466 (10)	1·485 (10)
Cl(4)–C(7)	1·758 (8)	1·768 (8)	C(2)–C(3)	1·296 (10)	1·308 (10)
O(1)–C(1)	1·380 (8)	1·373 (8)	C(3)–C(4)	1·528 (10)	1·501 (10)
O(1)–C(4)	1·418 (8)	1·428 (9)	C(4)–C(7)	1·534 (10)	1·536 (10)
O(2)–C(1)	1·179 (8)	1·180 (8)	C(5)–C(6)	1·476 (12)	1·481 (12)
O(3)–C(4)	1·408 (9)	1·399 (9)			

C(1)–O(1)–C(4)	110·1 (5)	110·7 (6)	O(1)–C(4)–C(3)	103·6 (6)	102·9 (6)
C(4)–O(3)–C(5)	119·2 (6)	119·8 (6)	O(1)–C(4)–C(7)	111·3 (6)	110·4 (6)
O(1)–C(1)–O(2)	121·6 (7)	123·3 (8)	O(3)–C(4)–C(3)	114·7 (6)	116·1 (7)
O(1)–C(1)–C(2)	107·3 (6)	107·4 (6)	O(3)–C(4)–C(7)	103·7 (6)	105·5 (6)
O(2)–C(1)–C(2)	131·1 (8)	129·3 (7)	C(3)–C(4)–C(7)	112·9 (6)	111·6 (6)
Cl(1)–C(2)–C(1)	121·3 (6)	122·5 (6)	O(3)–C(5)–O(4)	122·5 (8)	123·3 (8)
Cl(1)–C(2)–C(3)	129·1 (6)	129·9 (7)	O(3)–C(5)–C(6)	108·7 (8)	109·6 (7)
C(1)–C(2)–C(3)	109·5 (7)	107·6 (7)	O(4)–C(5)–C(6)	128·8 (9)	127·1 (8)
Cl(2)–C(3)–C(2)	131·0 (7)	128·9 (6)	Cl(3)–C(7)–Cl(4)	109·8 (5)	110·4 (5)
Cl(2)–C(3)–C(4)	119·7 (5)	119·7 (6)	Cl(3)–C(7)–C(4)	109·4 (5)	110·8 (6)
C(2)–C(3)–C(4)	109·3 (6)	111·4 (7)	Cl(4)–C(7)–C(4)	110·7 (6)	110·0 (5)
O(1)–C(4)–O(3)	110·9 (6)	110·4 (6)			

C(4)–O(1)–C(1)–C(2)	4·2 (8)	2·2 (8)
O(1)–C(1)–C(2)–C(3)	−5·1 (9)	−1·9 (9)
C(1)–C(2)–C(3)–C(4)	3·9 (9)	1·0 (9)
C(2)–C(3)–C(4)–O(1)	−1·4 (8)	0·3 (9)
C(1)–O(1)–C(4)–C(3)	−1·9 (8)	−1·6 (8)

The values correspond to the unprimed and primed molecules, respectively.

ment, three standard reflections (~6% uniform decay). Lp, decay, and absorption corrections (numerical integration, 362 sampling points), transmission factors 0·051–0·273, 4684 unique reflections measured, 2689 with $I \geq 2\sigma(I)$, where $\sigma^2(I) = S + 4(B_1 + B_2) + (0{\cdot}04S)^2$, S = scan, B_1 and B_2 = background counts. Structure by direct methods, refined by full-matrix least squares on F, H atoms in calculated positions (based on observed positions with $U_H \propto U_{\text{bonded atom}}$ and C—H = 0·98 Å), $w = 1/\sigma^2(F)$, scattering factors and anomalous-scattering corrections for Cl from *International Tables for X-ray Crystallography* (1974), locally written or locally modified versions of standard computer programs, final $R = 0{\cdot}062$, $wR = 0{\cdot}067$ for 2689 reflections with $I \geq 2\sigma(I)$, $S = 1{\cdot}071$, 272 parameters, isotropic type I extinction, $g = 0{\cdot}56\ (4) \times 10^4$, $R = 0{\cdot}117$ for all 4684 reflections, $\Delta/\sigma = 0{\cdot}02$ (mean), 0·21 (maximum), maximum final difference density −1·0 to 0·6 e Å^{-3} (all large peaks near Cl atoms).

Discussion. Final positional and equivalent isotropic thermal parameters (U_{eq} = 1/3 trace of diagonalized **U**) are given in Table 1, and geometrical data appear in Table 2.* Stereoviews of the two crystallographically independent molecules are shown in Fig. 1.

The compound (3*b*) is the acetate derivative of 3,4-dichloro-5-dichloromethyl-5-hydroxy-2(5*H*)-furanone (3*a*), a compound previously reported in the literature

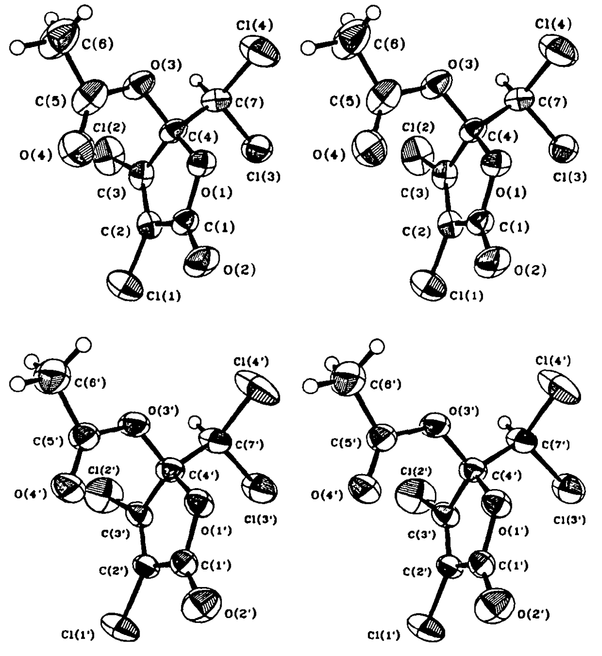

Fig. 1. Stereoviews of the two independent (3*b*) molecules; 50% probability thermal ellipsoids are shown for the non-hydrogen atoms. H atoms have been assigned artificially small thermal parameters for the sake of clarity. The *R* isomers are shown.

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* Lists of H-atom positions, anisotropic thermal parameters, torsion angles, and structure factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44718 (26 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

(Roedig & Märkl, 1960) and which gives the same acetate on treatment with potassium carbonate and acetic anhydride (Strömberg *et al.*, 1987). The direct formation of (3*b*) from (1) probably proceeds through anhydride-initiated cyclization of the intermediate (2).

The two crystallographically independent (3*b*) molecules (Fig. 1) are virtually identical. The five-membered ring is planar to within experimental error in the primed molecule, and planar to within 0·030 (8) Å in the unprimed molecule. The molecular geometry (Table 2) is normal, with mean distances $C(sp^2)$—Cl = 1·685 (7), $C(sp^3)$—Cl = 1·760 (9), C=O = 1·182 (4), $C(sp^2)$—O = 1·379 (11), $C(sp^3)$—O = 1·413 (12), C=C = 1·302 (8), $C(sp^2)$—$C(sp^2)$ = 1·475 (13), $C(sp^2)$—$C(sp^3)$ = 1·50 (2), and $C(sp^3)$—$C(sp^3)$ = 1·535 (1) Å. There are possible weak C—H···O hydrogen bonds involving the H atoms of the dichloromethyl groups: C(7)—H(7)···O(4′) ($\frac{3}{2}-x, y-\frac{1}{2}, \frac{1}{2}-z$) and C(7′)—H(7′)···O(4) ($1-x, -y, 1-z$) [H···O = 2·40, 2·41 Å; C···O = 3·311 (9), 3·23 (1) Å; C—H···O = 155, 141°]. The shortest intermolecular distance between non-hydrogen atoms is Cl(1′)···O(2) = 3·045 (6) Å.

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Structure–Reactivity Correlations of Benzoin Alkyl Ethers. Structures of 2-Methoxy-1,2-diphenylethanone (I) and 2-Isopropoxy-1,2-diphenylethanone (II)

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Abstract. (I): $C_{15}H_{14}O_2$, $M_r = 226·27$, triclinic, $P\bar{1}$, $a = 8·441$ (2), $b = 10·276$ (1), $c = 15·342$ (2) Å, $\alpha = 91·02$ (2), $\beta = 79·26$ (2), $\gamma = 105·88$ (2)°, $V = 1256·8$ (4) Å^3, $Z = 4$, $D_m = 1·209$ (flotation in KI), $D_x = 1·195$ g cm^{-3}, μ(Mo, $\lambda = 0·7107$ Å) = 0·44 cm^{-1}, $F(000) = 480$, $T = 293$ K, $R = 0·060$ for 1793 significant reflections. (II): $C_{17}H_{18}O_2$, $M_r = 254·83$, orthorhombic, $Pca2_1$, $a = 8·476$ (1), $b = 16·098$ (3), $c = 10·802$ (3) Å, $V = 1473·9$ (5) Å^3, $Z = 4$, $D_m = 1·161$ (flotation in KI), $D_x = 1·148$ g cm^{-3}, μ(Mo, $\lambda = 0·7107$ Å) = 0·41 cm^{-1}, $F(000) = 544$, $T = 293$ K, $R = 0·071$ for 867 significant reflections. Both (I) and (II) crystallize in a *cisoid* conformation for the carbonyl group and alkoxy groups. Compounds (I) and (II) are photostable on irradiation in the solid state in spite of the favourable conformation of the functional groups for intramolecular H abstraction. Absence of photoreaction of (I) and (II) in the solid state is rationalized in the light of unfavourable intramolecular geometry.

Introduction. Photolysis of benzoin alkyl ethers (I)–(III) in solution has been studied extensively (Tomioka & Izawa, 1980) and these were found to undergo only α-cleavage (Norrish type I) to form a benzoyl–benzyl radical pair which subsequently undergoes a free-radical reaction to give pinacol ethers and benzil as main products together with minor amounts of benzaldehyde. Irradiation of crystalline benzoin ethers results in no reaction. When the benzoin alkyl ethers were enclosed in a cyclodextrin cavity (β or γ) significant results were obtained on irradiation in the solid state. Under these conditions in all three cases products resulting from type I were absent whereas type II products were obtained in near quantitative yield (Dasaratha Reddy, Usha, Ramanathan & Ramamurthy, 1986). It has been suggested that the lack of type II products on irradiation of crystalline (I)–(III) is because of the absence of suitable conformers favourable for type II. Therefore crystallographic work

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