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Structure of 3-Acetyl-5-(α-methylbenzylidene)-2,4-oxolanedione, $C_{14}H_{12}O_4$

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Abstract. $M_r = 244{\cdot}2$, monoclinic, $P2_1/n$, $a = 4{\cdot}763\,(9)$, $b = 9{\cdot}785\,(5)$, $c = 24{\cdot}955\,(8)$ Å, $\beta = 92{\cdot}79\,(6)°$, $U = 1161{\cdot}67$ Å^3, $Z = 4$, $D_x = 1{\cdot}40$ Mg m^{-3}, $\lambda(\text{Mo}\,K\alpha) = 0{\cdot}71073$ Å, $\mu = 1{\cdot}11$ mm^{-1}, $F(000) = 512{\cdot}00$, $T = 298$ K. Final $R = 0{\cdot}043$ for 991 observed reflections. The molecule exists as the *endo*-enolic tautomer. It is essentially planar with the phenyl group *cis* to the lactone moiety. There is an intramolecular O—H···O hydrogen bond of 2·562 (4) Å. Structural differences between the title compound and 3-acetyl-5-benzylidene-2,4-oxolanedione are discussed.

Introduction. The presence of the 3-acyl-2,4-oxolanedione ring† in several biologically active molecules [such as tetramycin (Keller-Juslen *et al.*, 1982), terrestric acid (Jacobsen, Reffstrop, Cox, Holker & Boll, 1978) and pulvinones (Pattenden, 1977)] has prompted extensive studies on the tautomeric population of simpler analogues such as 3-acetyl-2,4-oxolanediones. Fig. 1 shows the four possible tautomers, all of which have been detected by spectroscopic methods with 5-methyl and 3-acetyl-5-methylene-2,4-oxolanediones (Gelin & Pollet, 1980). In sharp contrast, 3-acetyl-5-benzylidene-2,4-oxolanedione exists as one single tautomer, unambiguously determined as the *endo*-enol form (Fig. 1, *A*) by a crystallographic study (Mazhar-ul-Haque, Ahmed, Pollet & Horne, 1984).

Continued interest led us to consider 3-acetyl-5-(α-methylbenzylidene)-2,4-oxolanedione. In addition to the still unravelled geometry about the exocyclic double bond (Gelin & Hartmann, 1976), the presence of an additional methyl group was envisioned to have a considerable steric effect on the overall structure of the ring system.

Experimental. Crystal *ca* 0·21 × 0·21 × 0·55 mm, Enraf–Nonius CAD-4 diffractometer, take-off angle 5°, graphite-crystal-monochromatized Mo $K\alpha$ radiation, 25 reflections ($9 < \theta < 19°$) used to obtain cell dimensions by least-squares refinement, intensities of 2556 reflections measured, using ω–2θ scan, $\theta_{\max} = 25°$, range of hkl: −5 to 5, 0 to 11, 0 to 29; three standard reflections monitored at intervals of 9000 s showed no variation in intensities; 2045 unique and 991 observed reflections using $I > 2\sigma(I)$ criterion. Direct

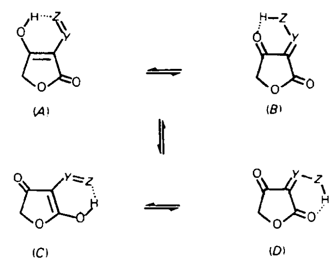

Fig. 1. Possible tautomeric forms for 3-substituted 2,4-oxolanediones.

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† 2,4-Oxolanedione is commonly referred to as 'tetronic acid'.

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methods, *MULTAN*78 (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978), $R_{\text{int}} = 0{\cdot}0035$ for merging equivalent reflections. F magnitudes used in E map and full-matrix least-squares refinement of non-H atoms with anisotropic temperature factors, and H atoms (taken from difference Fourier map) isotropically; final $R = 0{\cdot}0432$, $R_w = 0{\cdot}0429$; weighting scheme for function $w = 1{\cdot}5382/(\sigma^2|F_o| + 0{\cdot}000745F_o^2)$ used to minimize $\sum w\Delta F^2$, $S = 1{\cdot}58$. Max. peak height in final difference Fourier map $= 0{\cdot}189$ e Å^{-3}, $(\Delta/\sigma)_{\text{max}} = 0{\cdot}062$. No corrections for absorption and extinction factors. Form factors for non-H atoms those of Cromer & Mann (1968), for H atoms from Stewart, Davidson & Simpson (1965). Calculations on an IBM 3033 computer at the University of Petroleum & Minerals using *SHELX*76 (Sheldrick, 1976) programs.

Discussion. Fig. 2 is an *ORTEP* diagram (Johnson, 1976) of the molecule illustrating 30% probability ellipsoids for the non-H atoms and arbitrary spheres of radius 0·1 Å for H atoms together with the numbering scheme for the non-H atoms. The crystal packing is shown in Fig. 3. The positional parameters together with their U values for non-H atoms are given in Table 1. Table 2 contains the bond lengths and valence angles involving non-H atoms.*

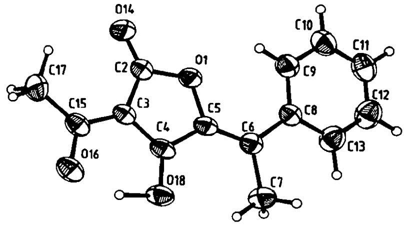

Fig. 2. *ORTEP* diagram of the $C_{14}H_{12}O_4$ molecule.

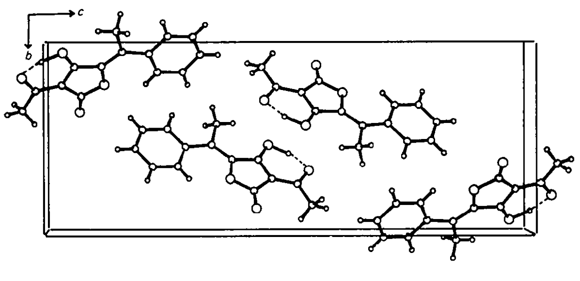

Fig. 3. The unit cell for $C_{14}H_{12}O_4$.

Table 1. *Fractional coordinates* (×10⁴), *with e.s.d.'s in parentheses, and equivalent isotropic thermal parameters* (Å² ×10³) *for the non-*H *atoms*

	x	y	z	U_{eq}*
O(1)	−1492 (5)	2742 (2)	6195 (1)	61
C(2)	−2108 (8)	2121 (4)	5702 (1)	58
C(3)	−284 (7)	2717 (3)	5322 (1)	53
C(4)	1348 (7)	3697 (3)	5590 (1)	57
C(5)	627 (7)	3727 (3)	6153 (1)	54
C(6)	1566 (7)	4482 (3)	6574 (1)	55
C(7)	3742 (10)	5546 (5)	6470 (2)	76
C(8)	606 (7)	4383 (3)	7128 (1)	55
C(9)	−1277 (9)	3408 (4)	7295 (2)	72
C(10)	−2135 (10)	3398 (5)	7817 (2)	81
C(11)	−1143 (10)	4334 (5)	8183 (2)	80
C(12)	716 (11)	5276 (6)	8031 (2)	92
C(13)	1590 (9)	5310 (4)	7509 (2)	80
O(14)	−3897 (6)	1265 (3)	5663 (1)	79
C(15)	−27 (7)	2423 (4)	4775 (1)	62
O(16)	1775 (5)	3100 (3)	4519 (1)	78
C(17)	−1720 (12)	1365 (5)	4490 (2)	82
O(18)	3213 (5)	4434 (2)	5373 (1)	73

* $U_{\text{eq}} = \frac{1}{3}$ (trace of orthogonalized U_{ij} matrix).

Table 2. *Bond lengths* (Å) *and angles* (°) *for non-*H *atoms, with e.s.d.'s in parentheses*

O(1)–C(2)	1·388 (4)	C(6)–C(8)	1·480 (4)
O(1)–C(5)	1·403 (3)	C(8)–C(9)	1·387 (5)
C(2)–C(3)	1·442 (4)	C(8)–C(13)	1·380 (5)
C(2)–O(14)	1·196 (4)	C(9)–C(10)	1·384 (5)
C(3)–C(4)	1·386 (4)	C(10)–C(11)	1·363 (6)
C(3)–C(15)	1·405 (4)	C(11)–C(12)	1·346 (6)
C(4)–C(5)	1·461 (4)	C(12)–C(13)	1·385 (6)
C(4)–O(18)	1·285 (4)	C(15)–O(16)	1·280 (4)
C(5)–C(6)	1·345 (4)	C(15)–C(17)	1·475 (5)
C(6)–C(7)	1·501 (5)		
C(2)–O(1)–C(5)	110·9 (2)	C(5)–C(6)–C(8)	126·1 (3)
C(3)–C(2)–O(1)	107·3 (3)	C(7)–C(6)–C(8)	117·1 (3)
O(1)–C(2)–O(14)	119·9 (3)	C(6)–C(8)–C(9)	124·0 (3)
C(3)–C(2)–O(14)	132·7 (3)	C(6)–C(8)–C(13)	119·4 (3)
C(2)–C(3)–C(4)	107·6 (3)	C(9)–C(8)–C(13)	116·7 (3)
C(2)–C(3)–C(15)	129·8 (3)	C(8)–C(9)–C(10)	120·8 (4)
C(4)–C(3)–C(15)	122·5 (3)	C(9)–C(10)–C(11)	121·3 (5)
C(3)–C(4)–C(5)	109·0 (3)	C(10)–C(11)–C(12)	118·8 (4)
C(3)–C(4)–O(18)	124·5 (3)	C(11)–C(12)–C(13)	121·0 (5)
C(5)–C(4)–O(18)	126·5 (3)	C(8)–C(13)–C(12)	121·6 (4)
O(1)–C(5)–C(4)	105·2 (3)	C(3)–C(15)–O(16)	118·1 (3)
O(1)–C(5)–C(6)	122·2 (3)	C(3)–C(15)–C(17)	122·8 (3)
C(4)–C(5)–C(6)	132·7 (3)	O(16)–C(15)–C(17)	119·1 (3)
C(5)–C(6)–C(7)	116·8 (3)		

The present structure closely resembles that of 3-acetyl-5-benzylidene-2,4-oxolanedione (hereinafter ABO) (Mazhar-ul-Haque *et al.*, 1984). Thus the molecule exists as the *endo*-enolic tautomer (Fig. 1, *A*), is essentially planar and has the phenyl group *cis* to the lactone moiety.

The dimerization observed with ABO is less evident in the present structure, where the crystal packing does not favour the formation of an intermolecular O–H···O′ link. {In fact, the O(18)···O′(18) separation of 2·809 Å is somewhat smaller than twice the normal

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* Lists of coordinates, bond lengths and angles involving H atoms, together with structure factors, anisotropic thermal parameters and deviations of atoms from mean planes have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39355 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

non-bonded contact radii between O atoms (Bondi, 1964), but this cannot plausibly be ascribed to hydrogen bonding in view of the sharp [92 (2)°] O′···H—O angle.} As a result, the *intra*molecular hydrogen bond which links O(16) and O(18), effectively forming a six-membered ring, is somewhat stronger than in the equivalent situation in ABO. [Thus, O(16)···H(18)—O(18) = 153 (2)°, O(16)···O(18) = 2·562 (4), O(16)···H(18) = 1·46 (4), and O(18)—H(18) = 1·18 (4) Å, compared with corresponding values of 139 (3)°, 2·751 (5), 1·98 (3), and 0·94 (3) Å for ABO].

The effects of the strengthened intramolecular hydrogen bond are reflected in the overall geometry of the hydrogen-bonded ring which, compared with the case of ABO, exhibits decreased internal ring angles about C(15) and C(4), a lengthened C(15)—O(16) distance, a shortened C(4)—O(18) distance, and significant ring puckering.

Other bond lengths and angles are comparable with those observed in related structures (Murray-Rust & Murray-Rust, 1978; Begley, Crombie, Havard & Reynolds, 1977).

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Structures Comparées de Deux Pyrroles: le Diphényl-3,5 Pyrroledicarboxylate-1,2 de Diéthyle, $C_{22}H_{21}NO_4$ (1), et le (Chloro-2 phényl)-3 Phényl-5 Pyrroledicarboxylate-1,2 de Diéthyle, $C_{22}H_{20}ClNO_4$ (2)

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Abstract. (1): $M_r = 363\cdot4$, *Pbca*, $a = 17\cdot213$ (3), $b = 18\cdot910$ (3), $c = 11\cdot968$ (3) Å, $V = 3895\cdot6$ (22) Å^3, $Z = 8$, $D_x = 1\cdot239$ Mg m^{-3}, Cu $K\alpha$, $\lambda = 1\cdot542$ Å, $\mu = 6\cdot13$ cm^{-1}, $F(000) = 1536$, $T = 291$ K, $R_w = 0\cdot081$ for 1762 signed reflections. (2): $M_r = 397\cdot9$, *Pbca*, $a = 16\cdot955$ (3), $b = 18\cdot487$ (4), $c = 13\cdot048$ (2) Å, $V = 4089\cdot7$ (37) Å^3, $Z = 8$, $D_x = 1\cdot293$ Mg m^{-3}, Cu $K\alpha$, $\lambda = 1\cdot542$ Å, $\mu = 17\cdot77$ cm^{-1}, $F(000) = 1664$, $T = 291$ K, $R_w = 0\cdot067$ for 3122 signed reflections. The modifications of the angles between the phenyl groups

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* L'auteur auquel toute correspondence doit être adressée.

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