

Crystal and molecular structure of (2*S*,5*S*)-2-*t*-butyl-5-phenyl-1,3-dioxolan-4-one, $C_{13}H_{16}O_3$

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1,3-Dioxolan-4-one / *Lactone*

Abstract. (2*S*,5*S*)-2-*t*-butyl-5-phenyl-1,3-dioxolan-4-one, $C_{13}H_{16}O_3$, MW = 220.27, monoclinic, $P2_1$, $a = 10.42(1)$, $b = 5.69(1)$, $c = 10.79(1)$ Å, $\beta = 109.8(1)^\circ$, $V = 602.0$ Å³, $Z = 2$, $D_c = 1.214$ Mg · m⁻³, $\lambda(\text{CuK}\alpha) = 1.5418$ Å, $\mu(\text{CuK}\alpha) = 7.04$ cm⁻¹, $F(000) = 236$, $T = 290(1)^\circ$, $R = 0.063$ for 684 observed reflections. The five-membered ring shows an envelope conformation with O(3) lying out of the plane of the ester group. The substituents are *cis*-related and occupy pseudoequatorial positions.

Introduction

The acid catalyzed condensation of α -hydroxy acids with aldehydes affords 1,3-dioxolan-4-ones, generally as a mixture of *cis*- and *trans*-diastereoisomers (Seebach et al., 1984). Attempts to establish the configuration of these compounds have been made by analysis of their NMR spectra, e.g. by comparison of chemical shifts (Pilgram and Zupan, 1977), long-range coupling constants (Asabe et al., 1973; Asabe et al. 1975) and by observation of nuclear Overhauser effect (NOE) (Seebach et al., 1984). Also CD-spectra of these compounds have been investigated (Połowski, 1983). Since the differences between chemical shifts and between coupling constants are

small, the stereochemical assignments on this basis are hazardous. The reaction of mandelic acid with pivalaldehyde gives the mixture of solid and liquid 2-*tert*-butyl-5-phenyl-1,3-dioxolan-4-ones. CD spectra suggest *trans*-configuration for the solid isomer (Połowski, 1983), however, on the basis of NOE studies the same compound was assigned as *cis* (Seebach et al., 1984). Our present investigation shows unequivocally that the crystalline diastereoisomer possesses *cis*-configuration.

Experimental

Colourless needles were grown from cyclohexane solution. Weissenberg photographs supplied preliminary cell dimensions and space-group data (absences $0k0$ for k odd.). Accurate cell dimensions were obtained by least-squares fitting of 18 reflections with high θ values. A crystal of approximate size $0.2 \times 0.9 \times 0.2$ mm was mounted along b -axis on a Hilger and Watts Y290 four-circle diffractometer. ω - 2θ scan was used with 30 steps of 0.02° and a count time per step 1 s. 1132 reflections were collected to $\theta_{\max} = 51^\circ$, of which 448 with $I < 2\sigma(I)$ were treated as unobserved in all subsequent calculations. Three standard intensities monitored every 50 measurements showed no significant change. Lorentz and polarization corrections were applied, but no absorption correction.

The structure was solved by the MULTAN program (Main, 1980) and refined by SHELX program (Sheldrick, 1976). The E-map showed clearly all non-hydrogen atoms. After full-matrix refinement (on F) of those atoms with anisotropic thermal parameters, the hydrogen atoms were included as 'riding' on their parent carbon atoms in calculated positions ($d_{C-H} = 1.08 \text{ \AA}$) with one common isotropic temperature factor. Methyl substituents were refined as rigid groups. The refinement converged at $R = 0.063$, $wR = 0.062$ for 684 observed reflections; $w = 1/[\sigma^2(F) + 0.005(F_0)^2]$. Max. least-squares $\Delta/\sigma = 1.2$ for methyl-group rotation, others < 0.3 . All peaks in final difference Fourier synthesis were within the range 0.23 and -0.25 e. \AA^3 . All calculations were performed on a DEC 10 computer.

Discussion

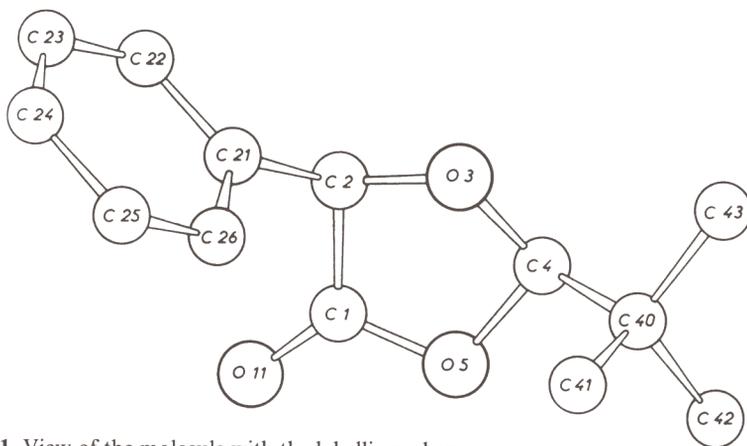
The final atomic parameters are given in Table 1. A list of bond lengths, bond angles and selected torsion angles has been deposited¹. A projection of the molecule with the atom labelling scheme is shown in Figure 1.

¹ Additional material to this paper can be ordered from the Fachinformationszentrum Energie-Physik-Mathematik, D-7514 Eggenstein-Leopoldshafen 2, FRG. Please quote reference no. CSD 51356, the names of the authors and the title of the paper

Table 1. Coordinates of non-hydrogen atoms ($\times 10^4$) with equivalent isotropic temperature factor

	x	y	z	U_{eq}
C(1)	-884(8)	5418	5734(7)	0.056
O(11)	-1674(5)	4499(19)	4751(4)	0.079
C(2)	-1040(6)	7596(20)	6442(6)	0.052
C(21)	-2397(6)	7842(19)	6626(6)	0.048
C(22)	-3253(7)	9734(23)	6086(7)	0.062
C(23)	-4522(7)	9883(23)	6273(8)	0.075
C(24)	-4939(7)	8160(22)	6969(7)	0.069
C(25)	-4079(7)	6270(23)	7470(7)	0.065
C(26)	-2830(7)	6083(21)	7293(7)	0.059
O(3)	33(4)	7396(17)	7668(4)	0.053
C(4)	1066(7)	5965(20)	7476(6)	0.053
C(40)	1834(6)	4650(20)	8686(6)	0.053
C(41)	895(8)	3165(21)	9201(7)	0.065
C(42)	2857(8)	3045(20)	8355(8)	0.080
C(43)	2598(8)	6429(23)	9724(8)	0.078
O(5)	322(5)	4404(17)	6399(4)	0.062

$$U_{eq} = [U_{11} + U_{22} + U_{33} + 2*U_{13}*\cos(\beta)]/3$$

**Fig. 1.** View of the molecule with the labelling scheme

The five-membered dioxolanone ring shows an envelope conformation with O(3) lying 0.392 Å out of the plane formed by remaining four atoms, while the ester group is essentially planar. Following Cremer and Pople (1975) notation the ring puckering parameters are: $q = 0.261$ Å and $\varphi = 11.08^\circ$. The phenyl and t-butyl substituents are *cis*-related and tend to occupy pseudoequatorial positions. The orientation of the phenyl ring with

Table 2. Deviations of atoms from least-squares planes (Å). E.s.d.'s < 0.015 Å. Asterisked atoms define planes

(1)	*C(1)	*C(2)	*O(3)	*C(4)	*O(5)	O(11)	
	-0.018	+0.111	-0.166	+0.149	-0.077	-0.121	
(2)	*C(1)	*C(2)	O(3)	*C(4)	*O(5)	O(11)	
	-0.031	+0.018	+0.392	-0.018	+0.031	-0.061	
(3)	*C(2)	*O(3)	*C(4)				
	0	0	0				
(4)	*C(21)	*C(22)	*C(23)	*C(24)	*C(25)	*C(26)	C(2)
	+0.015	-0.008	-0.003	+0.007	+0.001	-0.011	-0.003

Interplanar angles (°)

- (1)–(2) 7.3
 (1)–(3) 20.8
 (2)–(3) 28.0
 (2)–(4) 72.3

respect to the dioxolanone moiety is indicated by the angle 72.3°. The detailed analysis of planarity is given in Table 2.

The envelope conformation of five-membered ring is typical for analogous γ -lactones (Jeffrey et al., 1967; Harlow and Simonsen, 1976; Bocelli and Grenier-Loustalot, 1981), although it differs significantly from the three known structures of 1,3-dioxolan-4-ones derived from chloral (chloralides) which are nearly planar (Hashimoto et al., 1980; Brettle et al., 1983). This difference may result from dipole-dipole interactions of the trichloromethyl group with the dioxolanone ring and the *trans*-substitution of the rings of these chloralides.

Bond distances and angles show substantial agreement with those of the analogous compounds mentioned above. There are no particularly short intermolecular distances.

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References

- Asabe, Y., Takitani, S., Tsuzuki, Y.: Studies of saturated heterocyclic compounds. Preparation and PMR spectra of *cis* and *trans* 2,5-disubstituted 1,3-dioxolan-4-ones. *Bull. Chem. Soc. Jpn.* **46**, 661–662 (1973)
- Asabe, Y., Takitani, S., Tsuzuki, Y.: Studies of saturated heterocyclic compounds II. The preparation and PMR spectroscopic study of mono- and di-substituted-1,3-dioxolan-4-ones. *Bull. Chem. Soc. Jpn.* **48**, 966–970 (1975)
- Bocelli, G., Grenier-Loustalot, H. F.: The structure of 2-ammonio- γ -butyrolactone bromide. *Acta Crystallogr.* **B37**, 2106–2108 (1981)
- Brettle, R., Falshaw, C. P., King, T. J.: The stereochemistry of the tartaric acid chloralides. *J. Chem. Res. (S)*, 164–165 (1983)

- Cremer, D., Pople, J. A.: A general definition of ring puckering coordinates. *J. Am. Chem. Soc.* **97**, 1354–1358 (1975)
- Harlow, R. L., Simonsen, S. H.: The crystal structures of four 2,2-R,R'-4-benzyl-4-phenylbutanoic 1,4-lactones: (I) R = R' = H; (II) R = CH₃, R' = H, Z-configuration; (III) R = H, R' = CH₃, E-configuration; and (IV) R = R' = CH₃, all at -40°C. *Acta Crystallogr.* **B32**, 2137–2144 (1976)
- Hashimoto, M., Paulus, H., Weiss, A.: Crystal structure and phase transformation of trichloroethylidene trichloroacetic ester (chloralide), Cl₃CCHOCOCHOCCL₃. An X-ray and NQR study. *Ber. Bunsenges. Phys. Chem.* **84**, 883–890 (1980)
- Jeffrey, G. A., Rosenstein, R. D., Vlasse, M.: The crystal structure of D-galactono-γ-lactone. *Acta Crystallogr.* **22**, 725–733 (1967)
- Main, P.: MULTAN80. A system of computer programs for the automatic solution of crystal structures from X-ray diffraction data. Univ. of York and Louvain (1980)
- Pilgram, K., Zupan, M.: 1,3-dioxolan-4-ones and 1,3-oxathiolan-5-ones. Configuration of *cis* and *trans* isomers. *J. Heterocycl. Chem.* **13**, 1035–1037 (1977)
- Połośki, T.: Optical activity of lactones and lactams – I. Conformational dependence of the circular dichroism of 1,3-dioxolan-4-ones. *Tetrahedron* **39**, 3131–3137 (1983)
- Seebach, D., Naef, R., Caldenari, G.: α-alkylation of α-heterosubstituted carboxylic acids without racemization. EPC-syntheses of tertiary alcohols and thiols. *Tetrahedron* **40**, 1313–1325 (1984)
- Sheldrick, G. M.: SHELX76. Program system for crystal structure determination. Univ. of Cambridge (1976)