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Structure of *cis*-Tricyclo[6.3.0.0^{2,8}]undecane-3,11-dione

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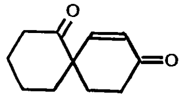
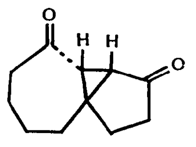
Abstract. $C_{11}H_{14}O_2$, $M_r = 178·23$, monoclinic, $P2_1/a$, $a = 11·566$ (2), $b = 8·369$ (1), $c = 9·533$ (1) Å, $\beta = 91·22$ (1)°, $V = 922·6$ (2) Å^3, $Z = 4$, $D_x = 1·283$ Mg m^{-3}, λ(Cu $K\alpha$) = 1·5418 Å, $\mu = 0·66$ mm^{-1}, $F(000) = 384$, $T = 293$ K, final $R = 0·038$ for 1371 unique reflections. The molecular configuration and the conformation of the title compound, a photoproduct from spiro[5.5]undec-7-ene-1,9-dione, have been determined. The ring junction at the C(1)—C(7) bond is *cis*. The seven-membered ring adopts an approximately chair conformation, and the five-membered ring has an envelope conformation. The molecules are packed in the crystal by van der Waals and C—H···O=C interactions.

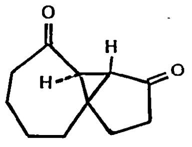
Introduction. Recently the photochemistry of the homoconjugated spiroketones has been initiated by our group (Kimura & Morosawa, 1981) and Oren & Fuchs (1986). We investigated the photochemistry of spiro[5.5]undec-7-ene-1,9-dione (1) by irradiation at ≥300 nm, and isolated one photoproduct (m.p. = 429–431 K) whose structure was assigned as *cis*- or *trans*-tricyclo[6.3.0.0^{2,8}]undecane-3,11-dione (2_c or 2_t) by NMR and IR data (Kimura & Morosawa, unpublished). In principle, there are two available modes of oxa-di-π-methane rearrangement, $\sigma 2_a + \pi 2_a$ and $\sigma 2_s + \pi 2_s$, yielding isomers in *trans* (2_t) and *cis* (2_c) configurations respectively. The structure of the photoproduct was confirmed as that of (2_c) by X-ray diffraction analysis.



(1)



(2_t)



(2_c)

Experimental. Crystals grown by slow evaporation from an ethanol solution, colorless plates developed {010} and elongated along **c**. Systematic absences $h0l$ for h odd, $0k0$ for k odd, space group $P2_1/a$. Crystal size 0·30 × 0·15 × 0·35 mm. Rigaku AFC-5 four-circle diffractometer. Lattice parameters determined with 18 reflections in the range $13 < 2\theta < 65°$ by least-squares method; intensities measured up to $(\sin\theta)/\lambda = 0·5761$ Å^{-1}, ω–2θ scan method [scan speed 4° min^{-1} in ω, scan range (2θ): 1·2° + 0·16° tanθ], Ni-filtered Cu $K\alpha$, 40 kV, 200 mA (rotating anode), background measured for 3 s on either side of the peak. Three standard reflections measured every 57 reflections, fluctuation within 1·3% in $|F|$. Lorentz and polarization corrections; no absorption correction. All 1371 unique reflections (ranging over $h = -12$ to 12, $k = 0$ to 9, $l = 0$ to 10) used for refinement; 1340 reflections larger than $1·0\sigma(F_o)$; $R_{\rm int} = 0·011$ for 80 $hk0$ reflections. Structure solved by *MULTAN*78, and refined (anisotropically) for non-H atoms by block-diagonal least squares: $\sum w(|F_o| - |F_c|)^2$ minimized, with $w = 1·0[\sigma(F_o)^2 + 0·0099|F_o| + 0·0004|F_o|^2]^{-1}$ for $|F_o| > 0$, $w = 3·475$ for $|F_o| = 0$; H-atom positions determined from a difference Fourier map, and refined isotropically by least squares. An extinction correction for 16 strongest reflections [$I_{\rm corr} = I_o(1 + 4·6 \times 10^{-5}I_c)$]. Final $R = 0·038$ for 1371 unique reflections, $wR = 0·063$, $S = 1·44$, $(\Delta/\sigma)_{\rm max}$ in the final refinement cycle 0·2; max. and min. $\Delta\rho$ in the final difference Fourier map 0·15 and −0·12 e Å^{-3}. Atomic scattering factors from *International Tables for X-ray Crystallography* (1974), computation carried out at the Crystallographic Research Center, Institute for Protein Research, Osaka University, and at the Okayama University Computer Center: programs *MULTAN*78 (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978), *HBLS*-V and *DAPH* (Ashida, 1973), *MOLCON* (Fujii, 1979) and *ORTEP* (Johnson, 1971).

Discussion. Final atomic parameters are listed in Table 1.* The thermal ellipsoids of the molecule are shown in

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* Lists of structure factors, anisotropic thermal parameters, H-atom parameters and bond lengths and angles involving H atoms have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44700 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Table 1. *Final atomic coordinates* (×10^4) *and equivalent isotropic thermal parameters with e.s.d.'s in parentheses*

$$B_{eq} = \tfrac{4}{3}\sum_i \beta_{ii}/a_i^{*2}.$$

	x	y	z	B_{eq}(Å^2)
O(1)	7008 (1)	3008 (1)	4872 (1)	4·93 (6)
O(2)	8044 (1)	6189 (1)	9711 (1)	4·09 (5)
C(1)	6551 (1)	4612 (2)	6754 (1)	2·58 (5)
C(2)	6595 (1)	3044 (2)	6030 (1)	2·81 (5)
C(3)	6161 (1)	1533 (2)	6684 (2)	3·37 (6)
C(4)	4844 (1)	1497 (2)	6870 (2)	3·99 (7)
C(5)	4405 (1)	2585 (2)	8017 (2)	3·64 (6)
C(6)	4397 (1)	4361 (2)	7681 (2)	3·58 (7)
C(7)	5551 (1)	5214 (2)	7597 (1)	2·60 (5)
C(8)	5506 (1)	7038 (2)	7634 (2)	3·45 (6)
C(9)	6686 (1)	7609 (2)	8183 (1)	3·41 (6)
C(10)	7245 (1)	6161 (2)	8867 (1)	2·84 (6)
C(11)	6631 (1)	4704 (2)	8374 (1)	2·44 (5)

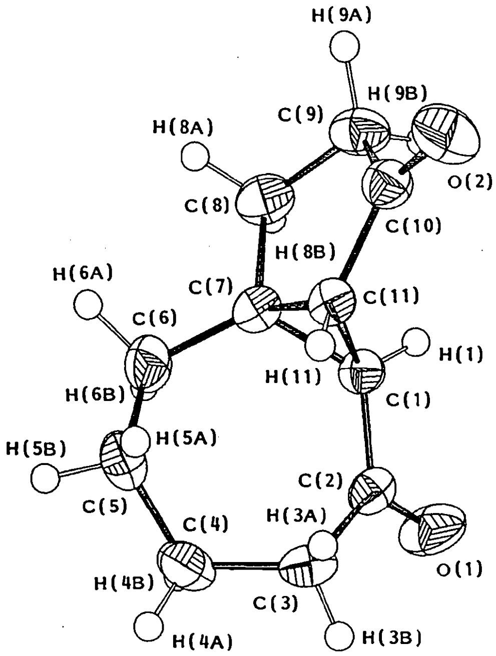

Fig. 1. View of the molecule with atom numbering. Ellipsoids of 50% probability are used for the non-H atoms; the H atoms are represented as spheres equivalent to $B = 1{\cdot}0$ Å^2.

Table 2. *Bond lengths* (Å) *and angles* (°) *with e.s.d.'s in parentheses*

O(1)—C(2)	1·213 (2)	C(5)—C(6)	1·520 (2)
O(2)—C(10)	1·213 (2)	C(6)—C(7)	1·517 (2)
C(1)—C(2)	1·484 (2)	C(7)—C(8)	1·528 (2)
C(1)—C(7)	1·509 (2)	C(7)—C(11)	1·501 (2)
C(1)—C(11)	1·547 (2)	C(8)—C(9)	1·528 (2)
C(2)—C(3)	1·501 (2)	C(9)—C(10)	1·515 (2)
C(3)—C(4)	1·538 (2)	C(10)—C(11)	1·483 (2)
C(4)—C(5)	1·519 (2)		
C(2)—C(1)—C(7)	125·3 (1)	C(1)—C(7)—C(11)	61·87 (9)
C(2)—C(1)—C(11)	120·4 (1)	C(6)—C(7)—C(8)	116·0 (1)
C(7)—C(1)—C(11)	58·80 (8)	C(6)—C(7)—C(11)	124·3 (1)
O(1)—C(2)—C(1)	117·6 (1)	C(8)—C(7)—C(11)	107·5 (1)
O(1)—C(2)—C(3)	119·9 (1)	C(7)—C(8)—C(9)	106·8 (1)
C(1)—C(2)—C(3)	122·5 (1)	C(8)—C(9)—C(10)	105·5 (1)
C(2)—C(3)—C(4)	113·9 (1)	O(2)—C(10)—C(9)	125·6 (1)
C(3)—C(4)—C(5)	114·7 (1)	O(2)—C(10)—C(11)	125·4 (1)
C(4)—C(5)—C(6)	115·8 (1)	C(9)—C(10)—C(11)	108·9 (1)
C(5)—C(6)—C(7)	118·0 (1)	C(1)—C(11)—C(7)	59·34 (8)
C(1)—C(7)—C(6)	123·8 (1)	C(1)—C(11)—C(10)	112·1 (1)
C(1)—C(7)—C(8)	111·9 (1)	C(7)—C(11)—C(10)	108·1 (1)

Table 3. *Selected torsion angles* (°)

(1) Seven-membered ring		
Endocyclic		
τ_1	C(7)—C(1)—C(2)—C(3)	−41·4 (2)
τ_2	C(1)—C(2)—C(3)—C(4)	67·3 (2)
τ_3	C(2)—C(3)—C(4)—C(5)	−72·1 (2)
τ_4	C(3)—C(4)—C(5)—C(6)	74·1 (2)
τ_5	C(4)—C(5)—C(6)—C(7)	−70·3 (2)
τ_6	C(5)—C(6)—C(7)—C(1)	49·5 (2)
τ_7	C(6)—C(7)—C(1)—C(2)	−7·1 (2)
Exocyclic		
τ_8	C(7)—C(1)—C(2)—O(1)	139·1 (1)
τ_9	C(11)—C(1)—C(2)—O(1)	−149·6 (1)
τ_{10}	C(6)—C(7)—C(1)—C(11)	−114·3 (2)
(2) Five-membered ring		
Endocyclic		
τ_{11}	C(11)—C(7)—C(8)—C(9)	11·1 (2)
τ_{12}	C(7)—C(8)—C(9)—C(10)	−17·1 (2)
τ_{13}	C(8)—C(9)—C(10)—C(11)	17·2 (2)
τ_{14}	C(9)—C(10)—C(11)—C(7)	−10·5 (2)
τ_{15}	C(10)—C(11)—C(7)—C(8)	−0·5 (1)
Exocyclic		
τ_{16}	O(2)—C(10)—C(11)—C(7)	167·6 (1)
τ_{17}	O(2)—C(10)—C(11)—C(1)	−128·9 (2)
τ_{18}	C(1)—C(11)—C(7)—C(8)	−105·9 (1)
(3) Three-membered ring		
τ_{19}	C(2)—C(1)—C(11)—C(10)	146·1 (1)

Fig. 1 with atomic numbering. Bond lengths and angles are listed in Table 2, and torsion angles characterizing the molecular conformation in Table 3.

The ring junction at the C(1)—C(7) bond is determined to be *cis* from the torsion angle $\tau_7 = -7{\cdot}1$ (2)°. The endocyclic torsion angles from τ_1 to τ_7 show that the seven-membered ring adopts an approximately chair conformation (Bocian & Strauss, 1977), as found in *trans*-tricyclo[6.3.0.0^{2,8}]undec-10-en-3-one (Zizuashvili, Abramson, Shmueli & Fuchs, 1982). The five-membered ring takes an envelope conformation: C(9) deviates by −0·272 (2) Å from the plane through C(10), C(11), C(7) and C(8). In the three-membered ring the C(1)—C(11) bond is longer than the C(1)—C(7) and C(7)—C(11) bonds. This lengthening may be ascribed to the electron-withdrawing effect of the carbonyl groups at C(2) and C(10): two C(sp^2)—C(sp^3) bonds, C(1)—C(2) and C(10)—C(11), connected to the C(1)—C(11) bond are shorter than the other C(sp^2)—C(sp^3) bonds, C(2)—C(3) and C(10)—C(9).

Molecular packing in the crystal is shown in Fig. 2. Two carbonyl groups take part in the C—H···O=C interactions between the molecules related by the 2_1 axes at $z = \frac{1}{2}$ and 1 to form a corrugated sheet parallel to (100) [C(9)···O(1) 3·326 (2), H(9*B*)···O(1) 2·42 (2) Å, C(9)—H(9*B*)···O(1) 157 (2), H(9*B*)···O(1)—C(2) 179·1 (5)°; C(11)···O(2) 3·478 (2), H(11)···O(2) 2·49 (2) Å, C(11)—H(11)···O(2) 178 (2),

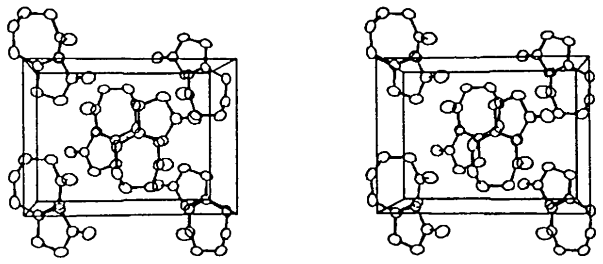

Fig. 2. Stereoscopic view of the molecular packing. The *a* axis points from left to right, the *b* axis upwards, and the *c* axis onto the plane of the paper; the H atoms are omitted.

H(11)···O(2)—C(10) 116·4 (5)°]. The sheets are stacked along **a** by van der Waals interactions with normal interatomic contacts.

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The Structure and Absolute Configuration of Acetomycin

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Abstract. $C_{10}H_{14}O_5$, $M_r = 214{\cdot}22$, orthorhombic, $P2_12_12_1$, $a = 14{\cdot}1084\,(6)$, $b = 10{\cdot}6443\,(3)$, $c = 7{\cdot}1970\,(1)$ Å, $V = 1080{\cdot}80\,(6)$ Å^3, $Z = 4$, $D_x = 1{\cdot}317$ Mg m^{-3}, Cu $K\alpha$, $\lambda = 1{\cdot}5418$ Å, $\mu = 0{\cdot}8571$ mm^{-1}, $F(000) = 456$, $T = 293$ K, $R = 0{\cdot}052$ for 816 observed [$3\sigma(I)$] Friedel pairs. The determined absolute configuration may be described as 3*S*,4*R*,5*R*, the five-membered ring having an envelope conformation, with the bulky substituents at *cis* positions. The bond lengths and angles are in agreement with those of the bromoacetoxy derivative.

Introduction. Acetomycin, (3*S*,4*S*,5*R*)-5-acetoxy-3-acetyl-3,4-dimethyldihydro-2(3*H*)-furanone, is an interesting antibiotic, both for its unique structure and for its biological properties. The correct molecular structure was established by Keller-Schierlein, Prelog and co-workers in a series of classical papers (Ettinger *et al.*, 1958; Keller-Schierlein, Mihailovic & Prelog, 1958; Bosshard, Goeckner & Keller-Schierlein, 1959; Bachmann, Gerlach, Prelog & Zahner, 1963). Even though it is not a first-line antibiotic, its broad activity, on bacteria, fungi (Ettinger *et al.*, 1958), mycobacteria (Uhr, Zeeck, Clegg, Egert, Fuher & Peter, 1985) and protozoa (Carrasco, 1984), makes it worthy of further study. The structural assessment and the relative and absolute configuration at the three chiral centres led us to undertake this study. Having finished our work, we received a preprint, from Professor Zeeck, with the absolute configuration of a bromoacetoxy derivative (Uhr *et al.*, 1985), both studies supporting the other's results.

Experimental. Samples were kindly supplied by Professors Prelog and Keller-Schierlein to whom we are indebted.* Cell constants obtained from a least-squares fit using 83 reflexions up to $\theta = 45°$ and Cu $K\alpha$

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* The sample shows an optical rotation of $[\alpha]_D^{20\,°C} = -157°$ (ethanol) as already described (Uhr *et al.*, 1985).

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