Fig. 1. Stereoscopic view of (2) with crystallographic atomic labelling.

Fig. 2. Stereo packing diagram of (2).

to which the H being abstracted lies outside the mean plane of the carbonyl group, is 65° for H_e, and 39° for H_a [in (1) the corresponding values are 45 and 35°, respectively]. The $\cos^2\tau$ dependence of abstraction, suggested by Wagner (1976), would reduce the relative reactivity of H_e by a factor of 6. The angle $\varDelta$, between the H in question and the C(7)—O(1) bond, is 73° for H_e, and 75° for H_a [in (1) the equivalent values are 90 and 66°, respectively], quite distorted from the ideal 90°. Abstraction of H_e would involve a chair-shaped six-membered transition state, in contrast to the boat geometry in compounds (1).

In compounds (1) H_β [H(9)] is in a favourable position for β-abstraction (although no such products are isolated), the O(1)···H_β distance being 2·6 Å, $\tau_\beta = 7–13°$, and $\varDelta_\beta = 82°$. In contrast, in (2), H(9) is 3·55 Å from O(1), τ_β is 28°, and $\varDelta_\beta = 30°$. Another β-H atom, H(163) on the methyl group C(16), is 2·60 Å away from O(1), its $\tau = 3°$, and $\varDelta = 83°$. The photochemical behaviour of compound (2) is not yet fully established.

The molecules of (2) form centrosymmetric carboxylic-acid dimers (Fig. 2) with O(2)···O(3) 2·62 Å. The two carboxyl O atoms, O(2) and O(3), are not very distinguishable; C(15)—O(2) is 1·276 (2) Å and C(15)—O(3) is 1·256 (2) Å. The same holds for their bond angles, C(3)—C(15)—O(2) 118·3 (2), C(3)—
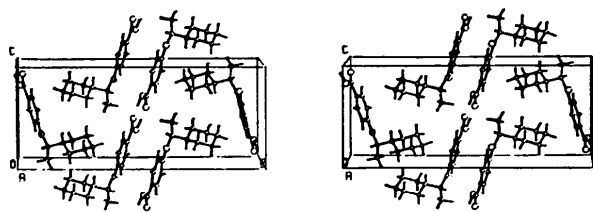
C(15)—O(3) 119·4 (1)°. However, a difference Fourier synthesis resolved only one carboxylic H atom, H(O), at 1·23 Å away from O(2). The hydrogen-bonding distance O(3)···H(O) is 1·39 (4) Å and the O(3)···H(O)—O(2) angle is 180°. The carboxyl group may be somewhat disordered, but the X-ray room-temperature data could not define this disorder more precisely. The angle between the carboxyl group and the aromatic ring is 1·4 (2)°.

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13-Oxatetracyclo[7.4.2.0³,¹⁵.0¹¹,¹⁴]pentadecane-6,12-dione

By M. Luyten, W. Luef, U. Beck and H. B. Buergi

Laboratorium für Chemische und Mineralogische Kristallographie, Universität Bern, Freiestrasse 3, CH-3012 Bern, Switzerland

Abstract. $C_{14}H_{18}O_3$, $M_r = 234\cdot29$, orthorhombic, *Pbca*, $a = 16\cdot409$ (5), $b = 13\cdot911$ (5), $c = 10\cdot506$ (8) Å, $V = 2398$ (3) Å^3, $Z = 8$, $D_m = 1\cdot288$, $D_x = 1\cdot298$ g cm^{-3}, Mo $K\bar{\alpha}$, $\lambda = 0\cdot71073$ Å, $\mu = 0\cdot841$ cm^{-1}, $F(000) = 1008$, $T = 295$ K, $R = 0\cdot056$ for 1154 observations. The structure analysis confirms

the identity of the title compound synthesized as a precursor for the all-*cis*-[5.5.5.5]fenestrane. It shows a chair–chair conformation for the eight-membered ring and envelope conformations for the two five-membered rings. The observed torsion angles agree to within 1·5° (r.m.s. deviation) with those calculated by force-field methods.

Introduction. The suitability of (2) as a precursor for the synthesis of (1) depends on the conformation of the cyclooctanone portion of (2) (Keese & Luyten, 1984). A structure determination was undertaken to confirm the identity of (2), to determine its conformation and to compare the conformation in the crystal with that calculated by force-field methods.

(1)   (2)

Experimental. Crystallization from concentrated dichloromethane diluted with *tert*-butyl methyl ether at room temperature yielded single crystals as colorless prisms; D_m by flotation in aqueous KI; single crystal 0·50 × 0·25 × 0·19 mm; Enraf–Nonius CAD-4 diffractometer; ω scan; lattice constants from 14 reflections in the range $11·8 \leq \theta \leq 15·7°$; 2114 unique reflections measured up to $\sin\theta/\lambda = 0·5941$ Å^{-1} ($0 \leq h \leq 18$, $0 \leq k \leq 16$, $0 \leq l \leq 12$); 1154 with $I > 3\sigma(I)$ used for refinement; 2 standard reflections, 0·7% loss; Lorentz and polarization, no absorption correction; structure solved by direct methods using the 240 largest E values ($E > 1·59$) for phase determination; full-matrix least-squares refinement based on F; positional and anisotropic thermal parameters of C and O atoms, scale factor and extinction coefficient refined; H positions calculated [$d(C-H) = 0·95$ Å]; $R = 0·056$, $wR = 0·046$ (unit weights), $S = 1·161$; max. $\Delta/\sigma = 0·02$; extinction coefficient = 8 (1) × 10^{-8} correlated to scale factor ($c = 0·70$); scattering factors and real and imaginary anomalous-dispersion corrections for neutral O and C from *International Tables for X-ray Crystallography* (1974), for H from Stewart, Davidson & Simpson (1965); final difference Fourier synthesis showed max. residual density of +0·454 and −0·213 e Å^{-3}, ~0·7–1·6 Å from atoms of lactone group. Programs: *MULTAN*11/82 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1982), *Structure Determination Package* (*SDP-Plus*) (Frenz, 1983); all computations on a PDP 11/34 computer.

Table 1. *Positional parameters and equivalent isotropic thermal parameters with e.s.d.'s in parentheses*

$$B_{eq} = 8\pi^2(U_{11} + U_{22} + U_{33})/3.$$

	x	y	z	B_{eq}(Å^2)
O(4)	0·2480 (2)	0·3076 (2)	0·4256 (3)	7·09 (8)
O(16)	0·2239 (2)	0·4524 (3)	0·3601 (3)	9·9 (1)
O(17)	−0·0530 (2)	0·2162 (3)	0·8138 (3)	8·7 (1)
C(1)	0·1115 (2)	0·2064 (3)	0·5585 (3)	4·24 (8)
C(2)	0·1978 (3)	0·1686 (3)	0·5402 (4)	6·4 (1)
C(3)	0·2514 (2)	0·2549 (4)	0·5467 (4)	5·8 (1)
C(5)	0·2299 (3)	0·4005 (3)	0·4516 (4)	6·4 (1)
C(6)	0·2190 (2)	0·4191 (3)	0·5886 (4)	5·8 (1)
C(7)	0·1387 (3)	0·4660 (3)	0·6218 (4)	6·1 (1)
C(8)	0·0755 (2)	0·3857 (3)	0·6085 (3)	4·16 (8)
C(9)	−0·0028 (3)	0·4045 (3)	0·6819 (4)	6·0 (1)
C(10)	−0·0707 (2)	0·3330 (4)	0·6540 (5)	6·8 (1)
C(11)	−0·0534 (2)	0·2335 (3)	0·7026 (4)	5·8 (1)
C(12)	−0·0358 (3)	0·1566 (3)	0·6074 (4)	6·4 (1)
C(13)	0·0538 (3)	0·1281 (3)	0·6049 (4)	5·9 (1)
C(14)	0·1216 (2)	0·2940 (2)	0·6474 (3)	3·57 (7)
C(15)	0·2137 (2)	0·3207 (3)	0·6440 (4)	4·48 (8)

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

O(4)–C(3)	1·469 (5)	C(6)–C(7)	1·512 (6)
O(4)–C(5)	1·353 (5)	C(6)–C(15)	1·490 (5)
O(16)–C(5)	1·207 (5)	C(7)–C(8)	1·530 (5)
O(17)–C(11)	1·193 (5)	C(8)–C(9)	1·520 (5)
C(1)–C(2)	1·523 (5)	C(8)–C(14)	1·538 (4)
C(1)–C(13)	1·523 (5)	C(9)–C(10)	1·522 (6)
C(1)–C(14)	1·545 (4)	C(10)–C(11)	1·504 (6)
C(2)–C(3)	1·491 (6)	C(11)–C(12)	1·492 (6)
C(3)–C(15)	1·505 (5)	C(12)–C(13)	1·523 (6)
C(5)–C(6)	1·474 (6)	C(14)–C(15)	1·557 (5)

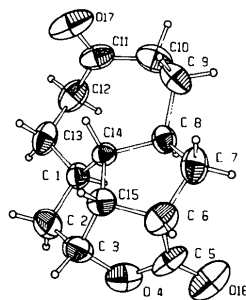|			
C(3)–O(4)–C(5)	108·1 (4)	C(7)–C(8)–C(14)	104·4 (3)
C(2)–C(1)–C(13)	111·8 (3)	C(9)–C(8)–C(14)	115·0 (3)
C(2)–C(1)–C(14)	104·5 (3)	C(8)–C(9)–C(10)	114·1 (3)
C(13)–C(1)–C(14)	116·0 (3)	C(9)–C(10)–C(11)	113·4 (4)
C(1)–C(2)–C(3)	105·4 (3)	O(17)–C(11)–C(10)	121·3 (5)
O(4)–C(3)–C(2)	109·8 (4)	O(17)–C(11)–C(12)	120·8 (5)
O(4)–C(3)–C(15)	105·6 (3)	C(10)–C(11)–C(12)	118·0 (4)
C(2)–C(3)–C(15)	106·1 (3)	C(11)–C(12)–C(13)	112·6 (4)
O(4)–C(5)–O(16)	115·4 (5)	C(1)–C(13)–C(12)	114·8 (3)
O(4)–C(5)–C(6)	113·0 (4)	C(1)–C(14)–C(8)	116·2 (3)
O(16)–C(5)–C(6)	131·5 (6)	C(1)–C(14)–C(15)	106·1 (3)
C(5)–C(6)–C(7)	114·0 (4)	C(8)–C(14)–C(15)	105·9 (3)
C(5)–C(6)–C(15)	103·1 (4)	C(3)–C(15)–C(6)	105·6 (3)
C(7)–C(6)–C(15)	104·8 (3)	C(3)–C(15)–C(14)	105·7 (3)
C(6)–C(7)–C(8)	104·8 (3)	C(6)–C(15)–C(14)	106·6 (3)
C(7)–C(8)–C(9)	113·6 (3)		

Fig. 1. *ORTEP* (Johnson, 1970) drawing of the molecule with atomic numbering.

Discussion. Fractional atomic coordinates are given in Table 1.* Bond lengths and angles involving nonhydrogen atoms with their e.s.d.'s are given in Table 2.

Stereochemistry. The relative configurations of C(1), C(8) and C(3), C(6) (see Fig. 1) correspond to those expected from the chemical work (Keese & Luyten, 1984). The two five-membered carbocycles are *cis* fused. The lactone is attached to the *endo* positions of C(3) and C(6) of the bicyclooctane fragment, the eight-membered ring to the *exo* positions of C(1) and C(8).

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* Lists of structure amplitudes, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42512 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 3. *Selected experimental torsion angles* (°); *MM2 results in parentheses*

E.s.d.'s are in the range 0·5–0·8°.

C(14)–C(1)–C(2)–C(3)	−31·8	(−33·9)
C(1)–C(2)–C(3)–C(15)	35·7	(37·2)
C(2)–C(3)–C(15)–C(14)	−24·8	(−26·3)
C(3)–C(15)–C(14)–C(1)	4·8	(5·5)
C(15)–C(14)–C(1)–C(2)	16·3	(17·4)
C(14)–C(8)–C(7)–C(6)	32·7	(34·4)
C(8)–C(7)–C(6)–C(15)	−37·7	(−38·7)
C(7)–C(6)–C(15)–C(14)	27·5	(28·2)
C(6)–C(15)–C(14)–C(8)	−7·2	(−6·9)
C(15)–C(14)–C(8)–C(7)	−15·6	(−16·9)
C(14)–C(8)–C(9)–C(10)	−68·5	(−71·1)
C(8)–C(9)–C(10)–C(11)	68·4	(68·2)
C(9)–C(10)–C(11)–C(12)	−109·4	(−106·8)
C(9)–C(8)–C(14)–C(1)	101·7	(103·5)
C(14)–C(1)–C(13)–C(12)	68·7	(70·8)
C(1)–C(13)–C(12)–C(11)	−66·1	(−68·3)
C(13)–C(12)–C(11)–C(10)	106·8	(106·9)
C(13)–C(1)–C(14)–C(8)	−102·8	(−103·1)

Conformation. Both cyclopentane rings of the bicyclooctane fragment are in the envelope conformation. The cyclooctanone ring shows a chair–chair conformation with approximate *mm2* symmetry (Table 3).

Energy-minimization calculations with the *MM2* force field (Allinger & Yuh, 1981) on the observed conformation lead to a very similar structure. On average, the absolute values of the observed C–C–C–C torsion angles are ~1° smaller than the calculated ones. Correspondingly, the observed C–C–C angles are 0·3° larger than the calculated ones (root-mean-square deviations are 1·5 and 0·9°, respectively). This indicates that the influence of molecular packing on the conformation of (2) is minimal. The packing arrangement is illustrated in Fig. 2.

A pronounced difference between observed and calculated geometries is found at the carbonyl carbon atom C(5). The observed and computed bond angles and their differences are respectively: O(4)–C(5)–C(6) 113·0, 109·9, 3·1°; C(6)–C(5)–O(16) 131·5, 126·1, 5·4°; O(4)–C(5)–O(16) 115·4, 124·0, −8·6°. These differences point to a systematic deficiency of the *MM2* force field which has been extensively documented elsewhere (Nørskov-Lauritsen, Bürgi, Hofmann & Schmidt, 1985).

This structure was solved during an introductory course into single-crystal X-ray structure determination.

Fig. 2. *ORTEP* (Johnson, 1970) stereoscopic view of the molecular packing.

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