

this type are also reported in similar compounds (Koetzle, Hamilton & Parthasarathy, 1972; Johnson & Kvik, 1972).

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## Structure of 1-Formyl-8-methoxy-3-methyl-5,6-dihydrobenz[*f*]isoquinolin-2(3*H*)-one\*

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**Abstract.** 8-Methoxy-3-methyl-2-oxo-2,3,5,6-tetrahydrobenz[*f*]isoquinoline-1-carbaldehyde, C<sub>16</sub>H<sub>15</sub>NO<sub>3</sub>, *M<sub>r</sub>* = 269.14, monoclinic, *P*2<sub>1</sub>/*a*, *a* = 7.509 (1), *b* = 10.123 (1), *c* = 17.391 (2) Å, β = 100.06 (1)°, *V* = 1301.63 (3) Å<sup>3</sup>, *Z* = 4, *D<sub>m</sub>*(floatation in KI solution) = 1.38, *D<sub>x</sub>* = 1.37 Mg m<sup>-3</sup>, λ(Mo *Kα*) = 0.7107 Å, μ = 0.1028 mm<sup>-1</sup>, *F*(000) = 568.0, *T* = 293 K, *R* = 0.037 for 1085 observed reflections. There is a short intramolecular C–H...O interaction owing to the preferred conformational orientation of the aldehyde group. This 'locked-in' conformation results in the formation of a seven-membered ring including the aromatic H atom [C...O = 2.898 (5), H...O = 2.58 Å; angle C–H...O = 99.7°]. The tricyclic moiety has two of its flanking rings planar while the central ring has a 'twist-boat' conformation.

**Introduction.** The title compound is an unusual derivative which resulted from a Reformatsky–Vilsmeier reaction on tetralone during an attempted preparation of a dihydronaphthaldehyde (Rao & Krishna Rao, 1986). The aim of the present investigation is to determine the stereochemical features of this novel intermediate.

**Experimental.** Crystal approx. 0.4 × 0.18 × 0.3 mm, Nonius CAD-4F-11M diffractometer, graphite-

monochromated Mo *Kα*, ω/2θ scan mode, scan speed 1° min<sup>-1</sup>, θ < 23.5°, *h* 0 to 8, *k* 0 to 11, *l* –19 to 19, 2041 reflections collected, 1085 judged significant (*|F<sub>o</sub>|* > 3σ*|F<sub>o</sub>|*), lattice parameters from 20 reflections

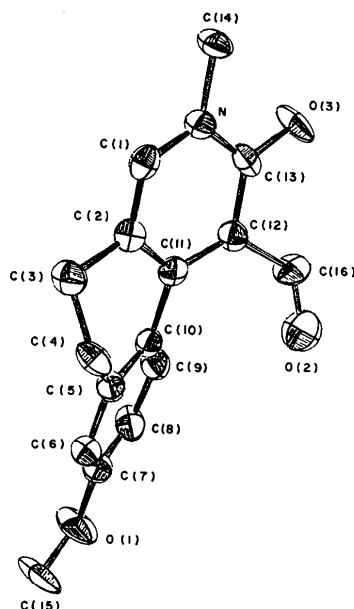


Fig. 1. ORTEP (Johnson, 1965) drawing of the molecule with crystallographic numbering scheme. Thermal ellipsoids are drawn at the 50% probability level.

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Table 1. Atomic coordinates ( $\times 10^4$ ) and equivalent isotropic thermal parameters for non-H atoms with e.s.d.'s in parentheses
$$B_{eq} = \frac{1}{3} \pi^2 \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	x	y	z	$B_{eq}(\text{\AA}^2)$
N	6815 (3)	5548 (2)	4609 (1)	2.70 (6)
O(1)	2161 (4)	3850 (3)	-14 (1)	5.11 (6)
O(2)	3975 (5)	7890 (2)	2376 (2)	5.82 (7)
O(3)	5312 (3)	7471 (2)	4652 (1)	4.04 (6)
C(1)	7325 (4)	4509 (3)	4194 (2)	2.85 (7)
C(2)	6668 (4)	4342 (3)	3422 (2)	2.69 (7)
C(3)	7320 (4)	3222 (3)	2972 (2)	3.23 (8)
C(4)	7425 (4)	3694 (3)	2148 (2)	3.36 (8)
C(5)	5558 (4)	4159 (3)	1775 (2)	2.84 (7)
C(6)	4802 (5)	3794 (3)	1014 (2)	3.29 (8)
C(7)	3042 (6)	4152 (4)	717 (2)	3.44 (8)
C(8)	2000 (6)	4852 (4)	1171 (2)	3.50 (8)
C(9)	2772 (5)	5243 (4)	1911 (2)	3.17 (8)
C(10)	4572 (5)	4928 (3)	2219 (2)	2.61 (7)
C(11)	5421 (5)	5267 (3)	3026 (2)	2.54 (7)
C(12)	5049 (5)	6401 (3)	3423 (2)	2.66 (7)
C(13)	5687 (5)	6540 (4)	4245 (2)	2.83 (7)
C(14)	7574 (6)	5693 (4)	5435 (2)	3.46 (8)
C(15)	3103 (8)	3085 (5)	-504 (3)	5.82 (11)
C(16)	4280 (6)	7624 (4)	3053 (2)	3.59 (8)

( $24 < 2\theta < 40^\circ$ ). Three standard reflections ( $\bar{4}00$ ,  $\bar{2}\bar{3}6$  and  $\bar{1}\bar{5}4$ ) every 2000 s, 3% variation in intensity. No correction for absorption, structure solved by direct methods using *MULTAN78* (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978). Full-matrix least-squares refinement (*LALS*; Gantzel, Sparks & Trueblood, 1961) of scale factor, positional and anisotropic thermal parameters for non-H atoms, and positional and isotropic thermal parameters for H atoms (located from a difference Fourier map), converged to  $R = 0.037$ ,  $wR = 0.042$ ,  $S = 0.95$ ,  $w(|F_o| - |F_c|)^2$  minimized,  $w = (3.5 + 1.0|F_o| + 0.015|F_c|^2)^{-1}$ ,  $(\Delta/\sigma)_{\max} = 0.1$ , final  $\Delta\rho$  excursions  $< |0.2| \text{ e \AA}^{-3}$ . No corrections for secondary extinction. Atomic scattering factors from *International Tables for X-ray Crystallography* (1974).

**Discussion.** Fig. 1 gives a perspective view of the molecule and crystallographic numbering of atoms. The atomic parameters along with their e.s.d.'s and equivalent isotropic thermal parameters, for the non-H atoms, are given in Table 1,\* while Table 2 gives the bond lengths and angles.

The preferred conformation of the aldehyde group allows an intramolecular interaction of the O atom O(2) with the aromatic C atom C(9), resulting in a 'locked-in' C—H...O moiety. This conformation avoids the dipolar repulsion between atoms O(2) and O(3). The rigidity of the tricyclic structure and the proximity

\* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51668 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. Bond distances ( $\text{\AA}$ ) and bond angles ( $^\circ$ ) with e.s.d.'s in parentheses

N—C(1)	1.367 (4)	C(4)—C(5)	1.513 (5)
N—C(13)	1.392 (4)	C(5)—C(6)	1.396 (4)
N—C(14)	1.458 (4)	C(5)—C(10)	1.397 (5)
O(1)—C(7)	1.361 (4)	C(6)—C(7)	1.380 (6)
O(1)—C(15)	1.427 (6)	C(7)—C(8)	1.399 (6)
O(2)—C(16)	1.190 (5)	C(8)—C(9)	1.374 (6)
O(3)—C(13)	1.240 (4)	C(9)—C(10)	1.401 (6)
C(1)—C(2)	1.357 (4)	C(10)—C(11)	1.477 (5)
C(2)—C(3)	1.506 (4)	C(11)—C(12)	1.392 (5)
C(2)—C(11)	1.415 (5)	C(12)—C(13)	1.435 (5)
C(3)—C(4)	1.526 (5)	C(12)—C(16)	1.466 (5)
C(1)—N—C(13)	121.3 (3)	C(6)—C(7)—C(8)	121.0 (4)
C(1)—N—C(14)	120.1 (3)	C(7)—C(8)—C(9)	119.3 (4)
C(13)—N—C(14)	118.5 (3)	C(8)—C(9)—C(10)	120.9 (4)
C(7)—O(1)—C(15)	118.0 (3)	C(5)—C(10)—C(9)	119.0 (3)
N—C(1)—C(2)	122.1 (3)	C(5)—C(10)—C(11)	118.2 (3)
C(1)—C(2)—C(3)	120.8 (3)	C(9)—C(10)—C(11)	122.6 (3)
C(1)—C(2)—C(11)	119.6 (3)	C(2)—C(11)—C(10)	116.5 (3)
C(3)—C(2)—C(11)	119.6 (3)	C(2)—C(11)—C(12)	118.6 (3)
C(2)—C(3)—C(4)	109.1 (3)	C(10)—C(11)—C(12)	124.9 (3)
C(3)—C(4)—C(5)	107.7 (3)	C(11)—C(12)—C(13)	120.9 (3)
C(4)—C(5)—C(6)	121.2 (3)	C(11)—C(12)—C(16)	125.2 (3)
C(4)—C(5)—C(10)	118.5 (3)	C(13)—C(12)—C(16)	113.1 (3)
C(6)—C(5)—C(10)	120.3 (3)	N—C(13)—O(3)	118.1 (3)
C(5)—C(6)—C(7)	119.3 (3)	N—C(13)—C(12)	116.9 (3)
O(1)—C(7)—C(6)	124.6 (3)	O(3)—C(13)—C(12)	125.0 (3)
O(1)—C(7)—C(8)	114.4 (3)		

Table 3. Short intramolecular C—H...O interactions ( $\text{\AA}$  and  $^\circ$ ) observed in different compounds

C...O	C—H	H...O	C—H...O	Reference
2.920	0.967	2.478	107.6	1
2.879	1.014	2.181	124.4	2*
2.931	1.019	2.182	128.9	2
2.850	0.983	2.025	140.0	2
2.835	0.923	2.415	107.7	3
2.820	1.071	2.419	100.6	3
2.802	0.916	2.183	124.2	4
2.797	0.949	2.381	106.1	4
2.898	0.961	2.580	99.7	5*

References: (1) Surcouf, Mornon & Malgrange (1978); (2) Chiesi Villa, Gaetani Manfredotti, Guastini, Casiraghi & Sartori (1979); (3) Brückner, Malpezzi, Prosyaniak & Bondarkenko (1985); (4) Molins, Rius, Miravittles & Blade-Font (1985); (5) present study.

\* These compounds form seven-membered rings involving C—H...O interactions.

of the aldehyde carbonyl group results in a seven-membered ring involving atoms C(10), C(11), C(12), C(16), O(2), H(9) and C(9) [C(9)...O(2) = 2.898 (5), H(9)...O(2) = 2.58 Å, angle C(9)—H(9)...O(2) = 99.7°]. Such short intramolecular C—H...O interactions are observed in several other structures as seen from Table 3. In a survey of short C—H...O and C—H...N interactions Taylor & Kennard (1982) conclude that these interactions are more attractive than repulsive and can reasonably be described as hydrogen bonds. However, as seen from Table 3 the C—H...O angle varies from 99.7 to 140° which indicates nonlinearity in such bonds. An examination of Table 2 reveals that the electron distribution is highly localized in the bonds of the seven-membered ring and the aldehyde group

[e.g. C(10)–C(11) = 1.477 (5) and C(12)–C(16) = 1.466 (6) Å] due to the formation of the short intramolecular C–H···O interaction.

The two flanking rings in the tricyclic moiety take up planar conformations while the central ring has a 'twist-boat' conformation. The molecules in the crystal structure are held together by van der Waals interactions.

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## 11β-Hydroxy-9β-estrone

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**Abstract.** C<sub>18</sub>H<sub>22</sub>O<sub>3</sub>, *M<sub>r</sub>* = 286.37, trigonal, *P*3<sub>2</sub>, *a* = 10.091 (1), *c* = 12.271 (1) Å, *V* = 1082.1 Å<sup>3</sup>, *Z* = 3, *D<sub>x</sub>* = 1.318 Mg m<sup>-3</sup>, λ(Cu *K*α) = 1.5418 Å, μ = 0.667 mm<sup>-1</sup>, *T* = 298 K, *F*(000) = 462, final *R* = 0.056 for 1468 observed reflections. The pattern of intermolecular interaction associated with 11β-hydroxy substitution differs from that observed in more potent estrogens.

**Introduction.** Compounds that bind to the estrogen receptor exhibit a remarkable variability in composition and stereochemistry. On the basis of an examination of a number of these compounds we have proposed that a phenolic ring is critical to the initiation of estrogen receptor binding (Duax, Griffin & Ebright, 1985). 11-Keto-9β-estrone was determined to be a more potent estrogen than its 11β-hydroxy analogue (Segaloff, Gabbard, Flores, Borne, Baker, Duax, Strong & Rohrer, 1980). The X-ray analysis of these compounds was undertaken as part of a program to define further the structural features that control estrogen receptor binding and activity. The X-ray studies were undertaken to verify the stereochemistry of the compounds and to determine how the different substitutions at

C(11) alter the overall shape of the steroids and their intermolecular interactions.

**Experimental.** Colourless crystals from acetone; crystal size: 0.48 × 0.72 × 0.8 mm; symmetry from photographs: *P*3<sub>1</sub> or *P*3<sub>2</sub>; *P*3<sub>2</sub> was chosen after the structure was solved on the basis of known enantiomorph; Enraf-Nonius CAD-4 diffractometer; graphite-monochromated Cu *K*α radiation; cell parameters refined by a least-squares fit of 24 reflections 71 ≤ 2θ ≤ 75°; 1481 unique reflections (0 ≤ *h* ≤ 13, 0 ≤ *k* ≤ 13, 0 ≤ *l* ≤ 15, 2θ ≤ 75°), 1468 observed reflections [*I* > 2σ(*I*)], corrected for Lp, no absorption correction applied: ω/2θ scan mode, scan angle (0.65 + 0.14 tan θ)°, scan aperture (2.00 + 0.15 tan θ) mm, maximum scan time 90 s, 3 orientation control reflections (1,  $\bar{1}$ ,  $\bar{10}$ ,  $\bar{173}$ ,  $\bar{711}$ ) monitored every 100 reflections, these reflections were used to check intensity decay; structure solved by direct methods (*MULTAN78*; Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978); full-matrix least-squares refinement on *F* for non-hydrogen atoms with anisotropic thermal parameters to minimize ∑*w*Δ<sup>2</sup>, where *w* = 1/σ<sub>*F*</sub><sup>2</sup>; all H atoms located in difference synthesis; further refinement with isotropic thermal