

carbonyl carbon in the phenacyl moiety [1.468 (8) and 1.493 (8) Å are the observed C—C distances in both the ligands]. The C=O distances, however, remain the same in both ligands [1.225 (7) and 1.212 (8) Å], since the electron drift from C=O to the Se atom is probably compensated by the electron drift towards C=O from the phenyl ring.

The bond lengths and angles around the C atoms have normal values. The C=O bond distance in both ligands is close to the double-bond distance of 1.19 Å. The bond lengths in the phenyl rings range from 1.353 (12) to 1.406 (11) Å. The torsional angles in the rings show the planarity of the rings to be within $\pm 2.8^\circ$.

References

- CROMER, D. T. & LIBERMAN, D. (1970). *J. Chem. Phys.* **53**, 1891–1898.
 CROMER, D. T. & MANN, J. B. (1968). *Acta Cryst.* **A24**, 321–324.
 DEXTER, D. D. (1972). *Acta Cryst.* **B28**, 49–54.
 GERMAIN, G., MAIN, P. & WOOLFSON, M. M. (1971). *Acta Cryst.* **A27**, 368–376.
 HANSEN, F., HAZELL, R. G. & RASMUSSEN, S. E. (1969). *Acta Chem. Scand.* **23**, 2561–2566.
 HERMODSSON, Y. (1967a). *Acta Chem. Scand.* **21**, 1313–1327.
 HERMODSSON, Y. (1967b). *Acta Chem. Scand.* **21**, 1328–1342.
 JOHNSON, C. K. (1976). *ORTEP*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee.
 MCCULLOUGH, J. D. (1937). *J. Am. Chem. Soc.* **59**, 789–794.
 STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.

Acta Cryst. (1983). **C39**, 622–624

Structure of (1*R**,13*R**,14*S**)-14-Hydroxy-6-methoxy-1,14-dimethyltetracyclo[11.3.1.0^{2,11}.0^{5,10}]heptadeca-2(11),5(10),6,8-tetraen-17-one, C₂₀H₂₄O₃

BY N. G. CHARLES, E. A. H. GRIFFITH, G. A. BONITZ, T. A. BRYSON AND E. L. AMMA†

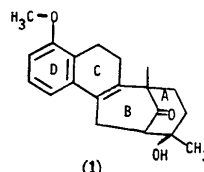
Department of Chemistry, University of South Carolina, Columbia, South Carolina 29208, USA

(Received 9 August 1982; accepted 5 January 1983)

Abstract. $M_r = 312.4$, triclinic, $P\bar{1}$, $a = 10.710$ (6), $b = 10.905$ (2), $c = 7.609$ (3) Å, $\alpha = 91.70$ (2), $\beta = 93.14$ (4), $\gamma = 68.69$ (4)°, $V = 826.4$ (8) Å³, $Z = 2$, $D_x = 1.26$, $D_m = 1.24$ (1) g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.71073$ Å, $\mu = 0.896$ cm⁻¹, $F(000) = 336$, $T = 291$ K. Final $R = 0.046$ with 1850 observed reflections. The structure consists of isolated molecules separated by ordinary van der Waals distances. The *A* ring exists in the chair conformation with the methyl group equatorial and the hydroxy group axial. The *B* ring approximates a sofa conformation. The carbon of the methoxy group is coplanar with the *D* ring.

Introduction. In comparing the activity and structure of natural steroids such as estrone and progesterone to those of bridged homosteroids a well-defined stereochemistry is essential. The subtle differences in these two groups of compounds are well documented in the literature (Lednicer & Mitscher, 1977). To understand better the conformational influences on activity of estrone derivatives (Johnson, David, Dehm, Hight, Warnoff, Wood & Jones, 1958) and the equivalent homologous compounds, one of us (TAB) has begun to investigate several fused and bridging homosteroid structures (Cargill, Bryson, Krueger, Kempf, McKenzie & Bordner, 1976). A classic synthon (1) used for

preparing hydrochrysenone compounds (Johnson, Korst, Clement & Dutta, 1960) is an obvious point for initiating such a study since there is no stereochemistry in the *B,C*-ring junction and this compound has a bridging aldol *A* ring. A crystal-structure determination of (1) was considered essential to the further synthetic development of this ring system.



Experimental. Title compound synthesized by known literature methods (Johnson *et al.*, 1960) and diffraction-quality crystals grown by slow evaporation of a secondary butanol solution over a period of a week; an approximately parallelepiped-shaped crystal of $\sim 0.70 \times 0.35 \times 0.63$ mm mounted in a glass capillary, faces $(\bar{2}02)$, $(\bar{2}02)$, $(10\bar{2})$, (102) , (010) , (101) ; Enraf-Nonius CAD-4 diffractometer, graphite monochromator, $\theta = 6.1^\circ$; 25 general reflections used in orientation matrix (checked every 24 h) and used for all parameter measurements; absorption corrections made, max. and min. transmission factors 0.983 and 0.957 (Frenz, 1980); variable scan speed with preliminary

† To whom correspondence should be addressed.

scan speed $4^\circ \text{ min}^{-1} (2\theta)$, $\omega-2\theta$ scan mode, $2\theta_{\text{max}} = 60^\circ$, hkl range = $-17-17$, $-17-17$, $0-12$; three standard reflections monitored every 100 reflections, decay $< 0.02 I$; 3500 independent hkl 's measured, 1850 used in structure solution and refinement, unobserved = $72 > F_{\text{min}} = 3.6$, data considered non-zero if $F^2 > 4\sigma(F^2)$, P factor = 0.030 in $\sigma(F^2) = [\sigma(I_{\text{raw}})^2 + (P \times I_{\text{raw}})^2]^{1/2}/Lp$.

The structure was solved with direct methods *via* MULTAN78 (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978; see also Main, 1976) in which the overall molecular geometry was utilized to generate starting phases. Without the molecular geometry the structure was not readily apparent, regardless of various levels of $\sin \theta$ data truncations. Initially, it appeared that there were two slightly different molecules in the unit cell, but they ultimately refined to one molecule in the asymmetric unit of $P1$. Structure refined by full-matrix least squares including anisotropic temperature factors for non-H atoms, absorption corrections and anomalous-dispersion corrections with weights based upon intensity statistics (Frenz, 1980), function minimized = $\sum_i w_i (|F_o|_i - |F_c|_i)^2$ where $w_i = 1/\sigma(F_o)^2$ (I); H atoms found from difference maps except for those on C(20) which were calculated (BONDAT, Stewart, 1979), H positional and thermal parameters not refined; final least squares (208 variables) performed on Amdahl V6 (CRYLSQ, Stewart, 1979) with f, f' and f'' from *International Tables for X-ray Crystallography* (1974) with weighting scheme 5 and F_{min} as above; final $R = 0.046$, $R_w = 0.056$; largest shift at end of refinement = 0.02σ , av. $< 0.01 \sigma$; error of observation of unit weight (EOUW) = 4.85 ; * final difference Fourier map qualitatively featureless.

Discussion. The non-H atomic coordinates are listed in Table 1.† Important bond distances and angles are in Table 2, together with least-squares planes and displacements from these planes and relevant torsion angles. An ORTEP (Johnson, 1970) drawing of the structure is shown in Fig. 1 and an ORTEP packing diagram is shown in Fig. 2.

The structure may be described as isolated molecules of (1), Fig. 1, separated by ordinary van der Waals distances, reflecting only non-bonded interactions be-

tween molecules, Fig. 2. The bond distances and angles are normal for this type of compound and show no unexpected values.

Table 1. Positional and equivalent isotropic thermal parameters for the non-H atoms with their e.s.d.'s in parentheses

$$B_{\text{eq}} = \frac{8}{3} \pi^2 \sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	x	y	z	$B_{\text{eq}}(\text{\AA}^2)$
O(1)	0.5285 (2)	-0.8722 (2)	0.3752 (3)	4.8 (1)
O(2)	0.1544 (2)	-0.0727 (2)	0.2135 (3)	4.3 (1)
O(3)	-0.1333 (2)	-0.0893 (2)	0.0763 (3)	3.91 (7)
C(1)	0.4972 (3)	-0.7917 (3)	0.2326 (4)	3.3 (1)
C(2)	0.5505 (3)	-0.8298 (3)	0.0681 (4)	3.8 (1)
C(3)	0.5096 (3)	-0.7407 (3)	-0.0674 (4)	3.9 (1)
C(4)	0.4181 (3)	-0.6143 (3)	-0.0429 (4)	3.3 (1)
C(5)	0.3644 (3)	-0.5749 (3)	0.1225 (4)	2.70 (7)
C(6)	0.4052 (3)	-0.6646 (3)	0.2609 (4)	3.0 (1)
C(7)	0.3401 (3)	-0.6266 (3)	0.4350 (4)	3.9 (1)
C(8)	0.2997 (3)	-0.4800 (3)	0.4740 (4)	3.8 (1)
C(9)	0.2339 (3)	-0.3954 (3)	0.3169 (4)	2.86 (7)
C(10)	0.2642 (3)	-0.4409 (3)	0.1526 (4)	2.71 (7)
C(11)	0.2027 (3)	-0.3597 (3)	-0.0096 (3)	2.93 (7)
C(12)	0.0933 (3)	-0.2245 (3)	0.0255 (4)	2.72 (7)
C(13)	0.1294 (3)	-0.1723 (3)	0.1991 (4)	2.9 (1)
C(14)	0.1322 (3)	-0.2581 (3)	0.3540 (4)	3.2 (1)
C(15)	-0.0099 (3)	-0.2648 (3)	0.3615 (4)	4.0 (1)
C(16)	-0.0607 (3)	-0.3058 (3)	0.1870 (4)	3.9 (1)
C(17)	-0.0521 (3)	-0.2222 (3)	0.0349 (4)	3.1 (1)
C(18)	-0.1046 (4)	-0.2619 (4)	-0.1385 (5)	4.4 (1)
C(19)	0.1700 (4)	-0.1974 (3)	0.5252 (4)	4.8 (2)
C(20)	0.6225 (4)	-1.0038 (3)	0.3552 (6)	5.7 (2)

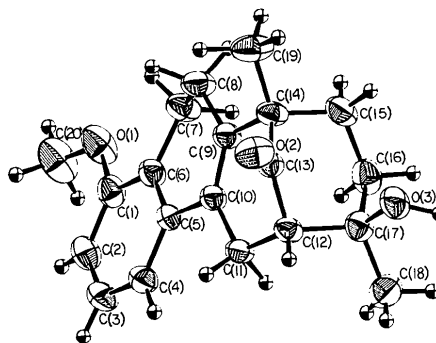


Fig. 1. An ORTEP drawing of the title molecule including H atoms.

The non-H-atom thermal ellipsoids are drawn at the 50% probability level. The H atoms were drawn with an arbitrary radius of 0.1 \AA . The notation is consistent with the tables in the text. The numbering is sequential starting from the D ring with C(1) bound to the methoxy group. The translation to the numbering of Johnson *et al.* (1960) is as follows: C(1)≡1', C(2)≡2', C(3)≡3', C(4)≡4', C(10)≡5'≡3, C(9)≡6'≡2, C(7)≡8', C(8)≡7', C(14)≡1, C(13)≡9, C(12)≡5, C(11)≡4, C(17)≡6, C(16)≡7, C(15)≡8. It is somewhat arbitrary at which end one should start naming this molecule as a steroid. One could (Duax, Weeks & Rohrer, 1976) name the anisole the A ring *etc.* The numbering translation would then be: C(1)≡4, C(2)≡3, C(3)≡2, C(4)≡1, C(6)≡5, C(5)≡10, C(7)≡6, C(8)≡7, C(9)≡8, C(10)≡9, C(11)≡11, C(12)≡12, C(13)≡13, C(14)≡14, C(15)≡15, C(16)≡16, C(17)≡17.

* Although this EOUW is somewhat high, it is not an uncommon situation with only light atoms and Mo radiation, *i.e.* a substantial number of weak reflections at high 2θ values which are beyond the Cu sphere. This refinement was carried out with unit weights, weighting scheme (I) and weighting scheme 5. The latter gave the best results in terms of R , R_w and EOUW.

† Lists of structure factors, anisotropic thermal parameters, H-atom positional and thermal parameters and bond distances and angles involving H atoms have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38349 (14 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. Molecular geometry

Bond distances (Å) and angles (°) with e.s.d.'s in parentheses

C(1)—C(2)	1.395 (5)	C(12)—C(13)	1.509 (4)
C(2)—C(3)	1.377 (5)	C(13)—C(14)	1.519 (4)
C(3)—C(4)	1.386 (4)	C(14)—C(9)	1.528 (4)
C(4)—C(5)	1.405 (4)	C(14)—C(15)	1.554 (5)
C(5)—C(6)	1.398 (4)	C(15)—C(16)	1.521 (5)
C(6)—C(1)	1.397 (4)	C(16)—C(17)	1.522 (5)
C(6)—C(7)	1.510 (4)	C(17)—C(12)	1.554 (5)
C(7)—C(8)	1.522 (5)	C(17)—C(18)	1.516 (5)
C(8)—C(9)	1.507 (4)	C(14)—C(19)	1.542 (5)
C(9)—C(10)	1.345 (4)	C(1)—O(1)	1.364 (4)
C(10)—C(5)	1.486 (3)	O(1)—C(20)	1.430 (4)
C(10)—C(11)	1.512 (4)	C(13)—O(2)	1.210 (4)
C(11)—C(12)	1.541 (3)	C(17)—O(3)	1.430 (3)
C(6)—C(1)—C(2)	120.9 (3)	C(11)—C(12)—C(13)	108.2 (2)
C(6)—C(1)—O(1)	115.2 (3)	C(11)—C(12)—C(17)	116.3 (3)
C(2)—C(1)—O(1)	124.0 (2)	C(13)—C(12)—C(17)	107.2 (2)
C(1)—C(2)—C(3)	118.9 (3)	C(12)—C(13)—C(14)	113.1 (3)
C(2)—C(3)—C(4)	121.4 (3)	C(12)—C(13)—O(2)	123.4 (3)
C(3)—C(4)—C(5)	120.0 (3)	C(14)—C(13)—O(2)	123.5 (3)
C(4)—C(5)—C(6)	119.0 (2)	C(13)—C(14)—C(9)	107.0 (2)
C(4)—C(5)—C(10)	121.5 (2)	C(13)—C(14)—C(15)	107.7 (2)
C(6)—C(5)—C(10)	119.5 (2)	C(13)—C(14)—C(19)	109.4 (3)
C(5)—C(6)—C(1)	119.8 (3)	C(9)—C(14)—C(15)	109.5 (3)
C(5)—C(6)—C(7)	119.3 (2)	C(9)—C(14)—C(19)	112.2 (2)
C(1)—C(6)—C(7)	120.7 (3)	C(15)—C(14)—C(19)	110.8 (3)
C(6)—C(7)—C(8)	112.1 (3)	C(14)—C(15)—C(16)	113.0 (3)
C(7)—C(8)—C(9)	113.1 (3)	C(15)—C(16)—C(17)	112.2 (3)
C(8)—C(9)—C(10)	120.6 (2)	C(16)—C(17)—C(12)	110.4 (2)
C(8)—C(9)—C(14)	116.9 (2)	C(16)—C(17)—C(18)	112.1 (3)
C(10)—C(9)—C(14)	122.5 (2)	C(16)—C(17)—O(3)	106.5 (2)
C(9)—C(10)—C(5)	120.7 (2)	C(12)—C(17)—C(18)	112.3 (3)
C(9)—C(10)—C(11)	122.8 (2)	C(12)—C(17)—O(3)	106.1 (3)
C(5)—C(10)—C(11)	116.4 (2)	C(18)—C(17)—O(3)	109.2 (2)
C(10)—C(11)—C(12)	115.1 (2)	C(1)—O(1)—C(20)	118.1 (3)

Least-squares planes with e.s.d.'s (all atoms weighted equally)
Equation of the plane of the form $Px + Qy + Rz = S$

Plane	Atoms	Max. deviation	Atoms out of plane
(1)	C(1)...C(6)	0.004 (3) Å	C(20) -0.03 (1) Å O(1) -0.02 (1)
(2)	C(5), C(9), C(10), C(11)	-0.009 (6)	
(3)	C(8), C(9), C(10), C(14)	0.002 (2)	

Angle between (2) and (3) is 0.46 (2)°

Torsion angles (°) with e.s.d.'s in parentheses

Ring A

C(17)—C(12)—C(13)—C(14)	-63.5 (5)	C(14)—C(15)—C(16)—C(17)	52.1 (6)
C(12)—C(13)—C(14)—C(15)	59.7 (5)	C(15)—C(16)—C(17)—C(12)	-54.9 (5)
C(13)—C(14)—C(15)—C(16)	-52.3 (5)	C(16)—C(17)—C(12)—C(13)	58.9 (4)

Ring B

C(14)—C(9)—C(10)—C(11)	1.4 (4)	C(11)—C(12)—C(13)—C(14)	-62.8 (5)
C(9)—C(10)—C(11)—C(12)	-5.0 (4)	C(12)—C(13)—C(14)—C(9)	58.1 (5)
C(10)—C(11)—C(12)—C(13)	33.8 (4)	C(13)—C(14)—C(9)—C(10)	26.4 (4)

Ring C

C(10)—C(5)—C(6)—C(7)	3.9 (4)	C(7)—C(8)—C(9)—C(10)	-28.6 (5)
C(5)—C(6)—C(7)—C(8)	-32.5 (5)	C(8)—C(9)—C(10)—C(5)	-0.8 (4)
C(6)—C(7)—C(8)—C(9)	43.6 (6)	C(9)—C(10)—C(5)—C(6)	14.2 (4)

The relative stereochemistry and conformation of the A ring is of particular concern to the synthetic chemist in that the aldol and Michael processes used to form (1) are reversible and the most stable bridged system was initially anticipated. However, it was not clear to us whether the A ring would preferentially exist in either a chair conformation with the C(17) methyl group *anti* to the C(14) methyl group or a boat conformation with the corresponding C(17) methyl group *syn* to the C(14) methyl group. It is clear from Fig. 1 that the A ring

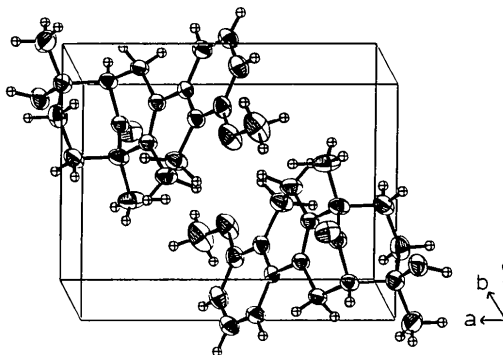


Fig. 2. An ORTEP drawing of the contents of the unit cell. Individual atoms are drawn as in Fig. 1. The origin of the unit cell is as indicated in the lower right-hand corner.

exists in the chair conformation with the C(17) methyl group equatorial [*anti* to C(19)] and the hydroxy group axial. The B ring approximates a sofa or half boat and the C ring approximates a half chair (see torsion angles in Table 2). The BC ethylenic ring juncture with its associated bonded atoms suffers a slight twist of 0.5 (1)° about the double bond. However, this approximate plane C(5), C(10), C(11), C(9), C(8), C(14) is tilted by ~4° away from the phenyl ring.

We wish to thank the University of South Carolina for funds to purchase the diffractometer.

References

- CARGILL, R. L., BRYSON, T. A., KRUEGER, L. M., KEMPF, J. V., MCKENZIE, T. C. & BORDNER, J. (1976). *J. Org. Chem.* **41**, 4096–4098.
- DUAX, W. L., WEEKS, C. M. & ROHRER, D. C. (1976). *Topics in Stereochemistry*, edited by N. ALLINGER & E. L. ELIEL, Vol. 9, pp. 271–383. New York: John Wiley & Sons.
- FRENZ, B. A. (1980). *Enraf-Nonius Structure Determination Package*. Version 17 with local modifications for the PDP-11/40. *International Tables for X-ray Crystallography* (1974). Vol. IV. Birmingham: Kynoch Press.
- JOHNSON, C. K. (1970). *ORTEP II*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.
- JOHNSON, W. S., DAVID, I. A., DEHM, H. C., HIGHT, R. J., WARNOFF, E. W., WOOD, W. D. & JONES, E. T. (1958). *J. Am. Chem. Soc.* **80**, 661–679.
- JOHNSON, W. S., KORST, J. J., CLEMENT, R. A. & DUTTA, J. (1960). *J. Am. Chem. Soc.* **82**, 614–622.
- LEDNICER, D. & MITSCHER, L. A. (1977). *Organic Chemistry of Drug Synthesis*, Ch. 10, pp. 155–207. New York: John Wiley & Sons.
- MAIN, P. (1976). *Crystallographic Computing Techniques*, edited by F. R. AHMED, pp. 96–105. Copenhagen: Munksgaard.
- MAIN, P., HULL, S. E., LESSINGER, L., GERMAIN, G., DECLERCQ, J. P. & WOOLFSON, M. M. (1978). *MULTAN 78. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univ. of York, England, and Louvain, Belgium.
- STEWART, J. M. (1979). Editor, the XRAY system. Tech. Rep. TR-445. Computer Science Center, Univ. of Maryland, College Park, Maryland.