1.9%) and 5134 reflections were classified as observed with $I > 3\sigma(I)$. ω–2θ scan technique was employed with an 8.0° $\min^{-1}$ scan rate. Weak reflections [$I < 10\sigma(I)$] were rescanned (maximum two rescans) and the counts accumulated to assure good counting statistics. Stationary background counts were recorded on each side of the reflection. Crystal and diffractometer stability was checked by monitoring three standard reflections every 150 reflections. Only random deviations (±4.3%) were observed over the course of data collection. No decay correction was applied. Empirical absorption correction, based on ψ scans, was applied with correction factors ranging from 0.84 to 1.00. The data were also corrected for Lorentz and polarization effects. The structure was solved by direct methods and Fourier synthesis, both of which are part of the *TEXSAN* program package (Molecular Structure Corporation, 1989) which showed an octahedral cluster sitting about a crystallographic center of inversion. H atoms were included in calculated positions.

During the final stages of refinement the positional and anisotropic thermal parameters of all non-H atoms were refined.* The final conventional agreement factors were $R = 0.033$, $wR = 0.036$ and $S = 1.22$ for the 5134 observed reflections and 487 variables. The function minimized was $\sum w(F_o - F_c)^2$ where $w = 1/\sigma^2(F_o)$ with $\sigma(F_o)$ from counting statistics. The maximum shift/e.s.d. in the last full-matrix least-squares cycle was less than 0.0004. The final difference Fourier map showed no peaks higher than 0.30 or deeper than -0.20 e Å^{-3}. All programs used in the structure solution and refinement are contained in the *TEXSAN* package (Molecular Structure Corporation, 1989). The plot was made using *ORTEP* (Johnson, 1976). The atomic scattering factors included with the software package are from *International Tables for X-ray Crystallography* (1974, Vol. IV). The final positional and displacement parameters for the metal anion are provided in Table 1. Table 2 contains selected bond geometry. Fig. 1 illustrates the metal coordination and the numbering scheme. Fig. 2 shows the unit-cell packing.

Related literature. A report of the tetramethylammonium salt has already appeared (Calabrese *et al.*, 1974).

KHW thanks the Robert A. Welch Foundation and the National Science Foundation for financial support of this work. REB thanks the National Science Foundation for a Predoctoral Fellowship.

References

CALABRESE, J. C., DAHL, L. F., CAVALIERI, A., CHINI, P., LONGONI, G. & MARTINENGO, S. (1974). *J. Am. Chem. Soc.* **96**, 2616–2618.
JOHNSON, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
Molecular Structure Corporation (1989). *TEXSAN. TEXRAY Structure Analysis Package*, version 5.0. MSC, 3200A Research Forest Drive, The Woodlands, TX 77381, USA.

---

* Lists of structure factors, anisotropic thermal parameters, H-atom parameters, full geometry and an *ORTEP* plot of the counter-anion have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55923 (72 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: HH1042]

Acta Cryst. (1993). C**49**, 1123–1125

Structure of 17β-Acetoxy-18-methyl-1-thia-*A*-norestra-3,9(10),11-trien-2-one

BY KENJI OKADA*

Research and Development Center, Ricoh Co. Ltd, Kouhoku-ku, Yokohama 223, Japan

AND HIROZO KOYAMA

Research Institute for Science and Technology, Kinki University, 3-4-1, Kowakae, Higashi Osaka 577, Japan

(*Received* 5 *December* 1991; *accepted* 15 *October* 1992)

Abstract. 18-Methyl-2-oxo-1-thia-*A*-norestra-3,9(10),11-trien-17β-yl acetate, $C_{19}H_{22}O_3S$, $M_r = 330.44$, triclinic, $P\bar{1}$, $a = 9.1267$ (12), $b = 11.955$ (1), $c = 8.783$ (1) Å, $\alpha = 93.08$ (1), $\beta = 117.70$ (1), $\gamma = 85.49$ (1)°, $V = 845.7$ (1) Å^3, $Z = 2$, $D_x = 1.298$ g cm^{-3}, λ(Mo $K\alpha$) = 0.7107 Å, $\mu = 1.94$ cm^{-1}, $F(000) = 352$, $T = 295$ K, $R = 0.054$, $wR = 0.047$ for 2920 observed reflections having $I \geq \sigma(I)$ (of 3632

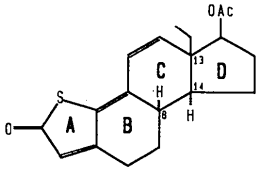
---

* To whom correspondence should be addressed.

0108-2701/93/061123-03$06.00

unique data). The steroid skeleton is slightly bent. Ring *A* is planar and rings *B* and *C* are in the envelope-like sofa conformations. Ring *D* has normal 14β-envelope conformation. The ring junction *C*/*D* is *trans*. The OAc side chain is planar and on the β face of ring *D*. The torsion angles H(14)—C(14)—C(8)—H(8) and C(16)—C(17)—O(2)—C(20) are 179.2 (16) and −81.8 (3)°, respectively. No unusual contacts are observed in the packing of the molecules.

Experimental. The title compound (I) was recrystallized from acetone as colorless prisms (m.p. 450–451 K).



(I)

The unit-cell dimensions and their e.s.d.'s were determined by least-squares refinement of the setting angles of 36 reflections ($6.1 \leq 2\theta \leq 21.6°$) measured on the automatic diffractometer. Intensity data were collected on a Hilger & Watts automatic four-circle Y 290 diffractometer controlled by a PDP 8 computer. Integrated intensities were measured for $2\theta < 55°$ by the ω–2θ-scan technique with Mo $K\alpha$ radiation. A standard reflection, $0\bar{6}2$, was monitored every 10 reflections and showed no significant variation over the data collection. 3632 independent reflections ($0 \leq h \leq 14$, $-15 \leq k \leq 15$, $-11 \leq l \leq 11$) were recorded, of which 2920 intensities having $I \geq \sigma(I)$ were considered observed. Intensities were corrected for Lorentz and polarization factors. No absorption corrections were applied since the specimen was considered to be sufficiently small (0.28 × 0.40 × 0.30 mm).

The structure was solved by direct methods using the automatic structure analysis program *DIRECTER* (Koyama & Okada, 1975; Okada & Koyama, 1991) based on the symbolic-addition method (Karle & Karle, 1966). The approximate coordinates of the molecule were refined by full-matrix least squares to minimize $\sum w[F_o(\mathbf{h}) - F_c(\mathbf{h})]^2$. The 22 H atoms were located from a difference Fourier synthesis. Inclusion of the H atoms with constant temperature factors $B = 2.5$ Å^2 in subsequent cycles of least-squares refinement reduced *R* to 0.054, $wR = 0.047$, $S = 0.54$ using 274 variables, and $(\Delta/\sigma)_{\max} = 0.28$ for 2920 reflections with $I \geq \sigma(I)$. Unit weights were applied. No further appropriate weighting scheme could be found from an analysis of ΔF values. Maximum and minimum peak heights in the final difference Fourier map were 0.11 and -0.03 e Å^{-3}. Atomic scattering factors used in all calculations were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV). All calculations were carried out with an NEC PC-9801RA personal computer using *DS*SYSTEM* (Okada, Okada & Koyama, 1990; Okada & Koyama, 1991).

Table 1. *Fractional atomic coordinates and equivalent isotropic thermal parameters* (Å^2)

$$B_{eq} = (4/3)\sum_i\sum_j \beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$$

	x	*y*	*z*	B_{eq}
S(1)	0.2329 (1)	0.3603 (1)	0.1087 (1)	4.26 (3)
O(1)	0.0005 (3)	0.2299 (2)	−0.1088 (3)	6.1 (1)
O(2)	0.7658 (2)	0.8648 (2)	0.5212 (3)	4.6 (1)
O(3)	1.0220 (3)	0.8595 (2)	0.5476 (3)	6.9 (1)
C(2)	0.0652 (4)	0.3177 (2)	−0.0907 (4)	4.7 (1)
C(3)	0.0278 (4)	0.4039 (3)	−0.2165 (4)	4.8 (1)
C(5)	0.1180 (3)	0.4936 (2)	−0.1581 (3)	4.1 (1)
C(6)	0.1087 (4)	0.5963 (3)	−0.2544 (4)	4.8 (1)
C(7)	0.2713 (4)	0.6544 (3)	−0.1715 (4)	4.3 (1)
C(8)	0.3252 (3)	0.6795 (2)	0.0187 (3)	3.5 (1)
C(9)	0.3392 (3)	0.5712 (2)	0.1110 (3)	3.5 (1)
C(10)	0.2401 (3)	0.4889 (2)	0.0229 (3)	3.7 (1)
C(11)	0.4617 (4)	0.5615 (2)	0.2912 (3)	3.8 (1)
C(12)	0.5588 (3)	0.6426 (2)	0.3824 (3)	3.8 (1)
C(13)	0.5443 (3)	0.7546 (2)	0.3062 (3)	3.5 (1)
C(14)	0.4879 (3)	0.7355 (2)	0.1122 (3)	3.6 (1)
C(15)	0.5095 (4)	0.8492 (2)	0.0552 (4)	4.4 (1)
C(16)	0.6678 (4)	0.8881 (3)	0.2074 (4)	5.0 (1)
C(17)	0.7072 (3)	0.8084 (2)	0.3561 (4)	4.1 (1)
C(18)	0.4213 (4)	0.8365 (2)	0.3418 (4)	4.1 (1)
C(20)	0.9274 (4)	0.8864 (2)	0.6048 (4)	4.8 (1)
C(21)	0.9681 (5)	0.9454 (3)	0.7679 (5)	6.4 (2)
C(22)	0.4319 (5)	0.8303 (3)	0.5180 (5)	5.8 (2)

The atomic coordinates and equivalent isotropic thermal parameters for non-H atoms are given in Table 1. Bond distances, angles and torsion angles are given in Table 2.† A stereoscopic view of the molecule with atom-numbering scheme is illustrated in Fig. 1, drawn with *ORTEP*II (Johnson, 1976), contained in *DS*SYSTEM*.

Related literature. The S—C bonds [1.790 (3) Å for S—C(2) and 1.767 (10) Å for S—C(10)] are considerably shorter than the normal value as observed in similar thiophenes: ethyl 2-amino-4,5,6,7-tetrahydrobenzo[*b*]thiophene-3-carboxylate (Larson & Simonsen, 1988). The nine atoms [C(2), C(3), C(5), C(8), C(9), C(10), C(11), C(12) and C(13)] of the steroid skeleton are coplanar and the largest deviation of these atoms is −0.11 (0) Å at C(13). The flattening of the steroid skeleton is often observed in androstenediones; *e.g.* 6α- and 6β-trifluoromethyl-substituted androstenedione (Eggleston & Lan-Hargest, 1990). Maximum distortion of bond angles occurs at C(13) in ring *D*, where C(14)—C(13)—C(17) is

---

† Lists of structure factors, anisotropic thermal parameters of non-H atoms, H-atom parameters, bond lengths and angles, and least-squares planes have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55739 (22 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AS0585]

Table 2. *Bond distances* (Å), *bond angles* (°) *and torsion angles* (°)

S(1)—C(2)	1.790 (3)	C(8)—C(14)	1.513 (4)
S(1)—C(10)	1.767 (3)	C(9)—C(10)	1.339 (3)
O(1)—C(2)	1.212 (4)	C(9)—C(11)	1.457 (3)
O(2)—C(17)	1.440 (4)	C(11)—C(12)	1.326 (4)
O(2)—C(20)	1.347 (3)	C(12)—C(13)	1.498 (4)
O(3)—C(20)	1.202 (5)	C(13)—C(14)	1.544 (4)
C(2)—C(3)	1.454 (5)	C(13)—C(17)	1.526 (4)
C(3)—C(5)	1.333 (4)	C(13)—C(18)	1.561 (4)
C(5)—C(6)	1.502 (5)	C(14)—C(15)	1.531 (4)
C(5)—C(10)	1.458 (3)	C(15)—C(16)	1.528 (4)
C(6)—C(7)	1.523 (5)	C(16)—C(17)	1.545 (5)
C(7)—C(8)	1.526 (4)	C(18)—C(22)	1.510 (6)
C(8)—C(9)	1.530 (4)	C(20)—C(21)	1.458 (5)

C(2)—S(1)—C(10)	92.0 (2)	C(9)—C(11)—C(12)	123.9 (3)
C(17)—O(2)—C(20)	117.4 (4)	C(11)—C(12)—C(13)	121.3 (2)
S(1)—C(2)—O(1)	122.6 (3)	C(12)—C(13)—C(14)	107.6 (2)
S(1)—C(2)—C(3)	108.5 (2)	C(12)—C(13)—C(17)	116.0 (2)
O(1)—C(2)—C(3)	128.9 (3)	C(12)—C(13)—C(18)	110.1 (3)
C(2)—C(3)—C(5)	115.5 (3)	C(14)—C(13)—C(17)	98.9 (3)
C(3)—C(5)—C(6)	128.4 (3)	C(14)—C(13)—C(18)	112.4 (2)
C(3)—C(5)—C(10)	114.3 (3)	C(17)—C(13)—C(18)	111.3 (2)
C(6)—C(5)—C(10)	117.3 (3)	C(8)—C(14)—C(13)	113.4 (3)
C(5)—C(6)—C(7)	111.7 (3)	C(8)—C(14)—C(15)	120.9 (2)
C(6)—C(7)—C(8)	110.8 (4)	C(13)—C(14)—C(15)	103.1 (2)
C(7)—C(8)—C(9)	110.0 (2)	C(14)—C(15)—C(16)	103.3 (3)
C(7)—C(8)—C(14)	114.3 (3)	C(15)—C(16)—C(17)	106.3 (3)
C(9)—C(8)—C(14)	108.5 (2)	O(2)—C(17)—C(13)	111.1 (3)
C(8)—C(9)—C(10)	118.9 (2)	O(2)—C(17)—C(16)	113.4 (3)
C(8)—C(9)—C(11)	118.4 (2)	C(13)—C(17)—C(16)	104.7 (3)
C(10)—C(9)—C(11)	122.7 (3)	C(13)—C(18)—C(22)	115.9 (3)
S(1)—C(10)—C(5)	109.7 (2)	O(2)—C(20)—O(3)	122.6 (3)
S(1)—C(10)—C(9)	125.5 (2)	O(2)—C(20)—C(21)	111.3 (4)
C(5)—C(10)—C(9)	124.8 (3)	O(3)—C(20)—C(21)	126.1 (4)

C(9)—C(10)—C(5)—C(6)	3.0 (4)	C(13)—C(14)—C(15)—C(16)	37.5 (3)
C(10)—C(5)—C(6)—C(7)	24.1 (4)	C(14)—C(15)—C(16)—C(17)	−11.6 (3)
C(5)—C(6)—C(7)—C(8)	−53.8 (3)	C(15)—C(16)—C(17)—C(13)	−18.7 (3)
C(6)—C(7)—C(8)—C(9)	56.5 (3)	C(16)—C(17)—C(13)—C(14)	40.7 (3)
C(7)—C(8)—C(9)—C(10)	−30.3 (4)	C(18)—C(13)—C(17)—O(2)	45.0 (3)
C(8)—C(9)—C(10)—C(5)	0.5 (4)	C(13)—C(17)—O(2)—C(20)	160.5 (2)
C(14)—C(8)—C(9)—C(11)	23.2 (3)	C(16)—C(17)—O(2)—C(20)	−81.8 (3)
C(8)—C(9)—C(11)—C(12)	2.3 (4)	C(17)—O(2)—C(20)—C(21)	178.9 (3)
C(9)—C(11)—C(12)—C(13)	2.5 (5)	C(17)—O(2)—C(20)—O(3)	−0.9 (5)
C(11)—C(12)—C(13)—C(14)	−31.2 (4)	C(12)—C(13)—C(18)—C(22)	40.0 (4)
C(12)—C(13)—C(14)—C(8)	58.1 (3)	C(14)—C(13)—C(18)—C(22)	159.9 (3)
C(13)—C(14)—C(8)—C(9)	−53.9 (3)	C(17)—C(13)—C(18)—C(22)	−90.1 (3)
C(17)—C(13)—C(14)—C(15)	−48.5 (3)		

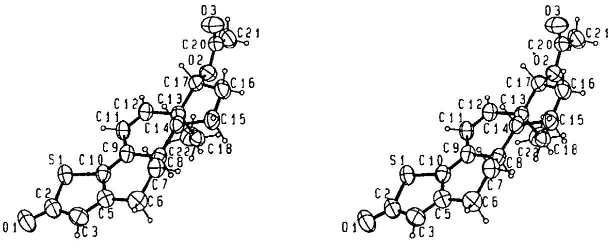


Fig. 1. A stereoscopic view of the molecules with the atom numbering viewed along the *c* axis. Thermal ellipsoids of the C and O atoms are drawn at 50% probability level. H atoms are shown with arbitrary radii.

98.9 (3)°. A similar bond angle was found in the following steroids: 6α-methyl-3,20-oxo-1,4,9(11)-pregnatrien-17α-yl acetate (Gałdecki, Grochulski, Wawrzak, Duax & Strong, 1990); 3β,20α-bis(dimethylamino)pregn-5-en-18-ol (Radhakrishnan, Viswamitra, Bhutani & Vaid, 1988). The plane of the OAc side chain and that of the ethyl side chain of C(13), C(18) and C(22) make angles of 80.3 (1) and 78.1 (2)°, respectively, with the steroid skeleton.

The authors are greatly indebted to T. Sato and H. Nakai, Shionogi Research Laboratory, for their technical assistance.

References

Eggleston, D. S. & Lan-Hargest, H.-Y. (1990). *Acta Cryst.* C**46**, 1686–1691.
Gałdecki, Z., Grochulski, P., Wawrzak, Z., Duax, W. L. & Strong, P. D. (1990). *Acta Cryst.* C**46**, 1498–1500.
Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
Karle, J. & Karle, I. L. (1966). *Acta Cryst.* **21**, 849–859.
Koyama, H. & Okada, K. (1975). *Acta Cryst.* A**31**, S-18.
Larson, S. B. & Simonsen, S. H. (1988). *Acta Cryst.* C**44**, 2035–2037.
Okada, K. & Koyama, H. (1991). *J. Appl. Cryst.* **24**, 1067–1970.
Okada, K., Okada, S. & Koyama, H. (1990). *Acta Cryst.* A**46**, C-70.
Radhakrishnan, R., Viswamitra, M. A., Bhutani, K. K. & Vaid, R. M. (1988). *Acta Cryst.* C**44**, 1820–1823.

Acta Cryst. (1993). C**49**, 1125–1127

1-[3-(3,4-Methylenedioxyphenoxy)propyl]-4-phenylpiperazine Monohydrochloride

Kojun Okamoto, Satoshi Fujii and Ken-ichi Tomita*

Faculty of Pharmaceutical Sciences, Osaka University, 1-6, *Yamada-Oka, Suita City, Osaka* 565, *Japan*

(*Received* 23 *May* 1991; *accepted* 15 *February* 1993)

Abstract. 1-[3-(Benzo[1,3]dioxol-5-yloxy)propyl]-4-phenylpiperazinium chloride, $C_{20}H_{25}N_2O_3^+.Cl^-$, M_r = 376.5, orthorhombic, *Pbca*, $a = 17.615\ (1)$, $b = 15.400\ (2)$, $c = 13.786\ (2)$ Å, $V = 3739.9\ (8)$ Å^3, $Z = 8$, $D_x = 1.339$ Mg m^{-3}, λ(Cu $K\alpha$) = 1.5418 Å, $\mu = 1.998$ mm^{-1}, $F(000) = 1600$, $T = 293$ K, final R =

---

* Author to whom correspondence should be addressed.

0108-2701/93/061125-03$06.00