References

ANDREWS, L. (1974). *FLINUS*. Brookhaven National Laboratory, Upton, NY 11973, USA.

BHATT, M. V. & KAMATH, K. M. (1968). *J. Chem. Soc. B*, pp. 1036–1044.

BOWDEN, K. & TAYLOR G. R. (1971). *J. Chem. Soc. B*, pp. 1390–1394.

BUSING, W. R., MARTIN, K. O. & LEVY, H. A. (1962). *ORFLS*. Report ORNL-TM-305. Oak Ridge National Laboratory, Tennessee, USA.

BUSING, W. R., MARTIN, K. O. & LEVY, H. A. (1964). *ORFFE*. Report ORNL-TM-306. Oak Ridge National Laboratory, Tennessee, USA.

DELETTRE, J. (1969). *C. R. Acad. Sci. Sér. C*, **269**, 103–104.

GLICK, M. (1975). *SYNCOR*. Wayne State Univ., Detroit, MI 48202, USA. Personal communication.

GRIFFE, M., DURANT, F. & PIERET, A. F. (1972). *Bull. Soc. Chim. Belg.* **81**, 319–332.

HOLLANDER, F. (1975). *ABSOR*. Brookhaven National Laboratory, Upton, NY 11973, USA.

International Tables for X-ray Crystallography (1974). Vol. IV, pp. 72–98. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)

JOHNSON, C. K. (1970). *ORTEPII*. Report ORNL-3794, revised. Oak Ridge National Laboratory, Tennessee, USA.

KUNDU, M. L. & CHAKRAVORTY, S. C. (1967). *Indian J. Phys.* **41**, 547–549.

LALANCETTE, R. A., CEFOLA, M., HAMILTON, W. C. & LA PLACA, S. J. (1967). *Inorg. Chem.* **6**, 2127–2134.

LALANCETTE, R. A., SLIFER, P. B. & THOMPSON, H. W. (1989). *Acta Cryst.* **B45**, 596–597.

LEISEROWITZ, L. (1976). *Acta Cryst.* **B32**, 775–802.

MAIN, P., FISKE, S. J., HULL, S. E., LESSINGER, L., GERMAIN, G., DECLERCQ, J.-P. & WOOLFSON, M. M. (1980). *MULTAN80. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univs. of York, England, and Louvain, Belgium.

PLASKUDA, H. (1874). *Chem. Ber.* **7**, 986–988.

PLASCUDA, H. & ZINCKE, TH. (1873). *Chem. Ber.* **6**, 906–910.

SHELDRICK, W. S. & TROWITSCH, W. (1983). *Z. Naturforsch. Teil B*, **38**, 220–225.

SHIONO, R. (1971). *GEOM*. Univ. of Pittsburgh, PA 15260, USA.

TEMPLETON, L. K. & TEMPLETON, D. H. (1973). Proc. Am. Crystallogr. Assoc. Meet. Abstr., Ser. 2, Vol. 1, p. 143.

TYMAN, J. H. P. & NAJAM, A. A. (1977) *Spectrochim. Acta*, **33A**, 479–485.

VANDERHOFF, P. A., THOMPSON, H. W. & LALANCETTE, R. A. (1986). *Acta Cryst.* **C42**, 1766–1769.

ZALKIN, A. (1962). *FORDAP*. Univ. of California, Berkeley, CA 94720, USA.

6α- and 6β-Trifluoromethyl-Substituted Androstenedione

BY DRAKE S. EGGLESTON* AND HSUAN-YIN LAN-HARGEST†

Department of Physical and Structural Chemistry and Department of Medicinal Chemistry, Smith Kline & French Laboratories, L-950, PO Box 1539, King of Prussia, PA 19406–0939, USA

Abstract. 6β-Trifluoromethyl-4-androstene-3,17-dione (I), C$_{20}$H$_{25}$F$_3$O$_2$, M_r = 354·42, orthorhombic, $P2_12_12_1$, a = 8·123 (3), b = 10·348 (3), c = 21·725 (11) Å, V = 1826·1 (15) Å^3, Z = 4, D_x = 1·289 Mg m^{-3}, λ(Mo Kα) = 0·71073 Å, μ = 0·0964 mm^{-1}, F(000) = 752, T = 293 K, R = 0·052, wR = 0·061 for 930 observations. 6α-Trifluoromethyl-4-androstene-3,17-dione (II), C$_{20}$H$_{25}$F$_3$O$_2$, M_r = 354·42, tetragonal, $P4_12_12$, a = 10·896 (2), c = 29·569 (6) Å, V = 3510·7 (6) Å^3, Z = 8, D_x = 1·341 Mg m^{-3}, λ(Cu Kα) = 1·54184 Å, μ = 0·8647 mm^{-1}, F(000) = 1504, T = 293 K, R = 0·065, wR = 0·093 for 1576 observations. The novel 6β steroid (I) was prepared from a photochemical rearrangement of a dienoltriflate; its α epimer (II) was prepared from acid treatment of (I). The overall conformation of (I) is nearly identical to that of the parent molecule, androst-4-ene-3,17-dione, to which the structures of both (I) and (II) are conveniently compared. The A-ring conformation of (I) may be described either as a (1α-2β) half-chair or as a 1α-sofa; A-ring asymmetry parameters are $\Delta C_2^{1,2}$ = 14·2, ΔC_s^1 = 12·5 with an average internal ring torsion angle of 26·9°. The D-ring conformation is a 14α-envelope; $\Delta C_s(14)$ = 15·6. The A-ring bowing angle is 19·2°. For (II) a disordered A ring with two half-occupancy positions for C(2) is found. The A-ring conformation thus may be described both as a 2α- and a 2β-sofa; A-ring asymmetry parameters are $\Delta C_s(2α)$ = 6·5, $\Delta C_s(2β)$ = 2·4; average torsion angle within the ring = 24·4 (2α) or 24·2° (2β). The B and C rings adopt normal chair conformations; the D ring is a 14α-envelope with $\Delta C_s(14)$ = 9·2. The steroid bowing angle is 43·9° with inclusion of all A-ring atoms.

Introduction. In conjunction with an interest in the design of inhibitors for the enzyme steroid 5α-reductase, the 6β-trifluoromethyl-substituted andro-

---

* Department of Physical and Structural Chemistry.

† Department of Medicinal Chemistry.

    © 1990 International Union of Crystallography

stenedione (I) was prepared *via* the novel photochemical rearrangement of a steroidal dienoltriflate (Lan-Hargest, Elliott, Eggleston & Metcalf, 1987). The thermodynamically more stable equatorially substituted 6α epimer (II) was obtained *via* acid treatment of (I). Beyond proving unambiguously the structures of these novel compounds, our interest focused on the effects which α or β substitution of this bulky group at position 6 might induce upon steroidal conformation, particularly features of the *A* ring. To this end, we present comparisons to some androst-4-ene-3-ones in the literature.

(I)   (II)
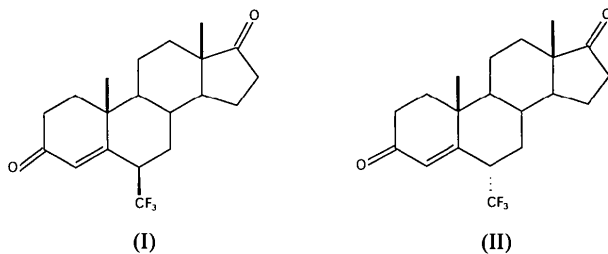
Experimental. For (I), weakly diffracting colorless tablet from ethyl acetate approximately $0.10 \times 0.24 \times 0.20$ mm on edge, mounted with epoxy on a glass fiber. Cell constants from a least-squares analysis of 25 reflections $[30 \le 2\theta(\text{Mo}) \le 35°]$ measured on the diffractometer. Data collected on an Enraf–Nonius CAD-4 diffractometer equipped with graphite monochromator; variable speed $\omega–2\theta$ scans. Systematic absences: $h00$, $0k0$, $00l$ for h,k,l odd, respectively; 2524 reflections for $2\theta \le 56°$, $0 \le h \le 10$, $0 \le k \le 13$, $0 \le l \le 28$; Lorentz–polarization correction, no systematic fluctuations in reflections 081, $\overline{3},4,13$, 547, monitored at the beginning, end and every 3 h during data collection (13 times): max. deviation in $|F_o|$ 2·5, 3·9 and 3·0%, respectively; mean values of $|F_o|$ 121·0 (15), 94·0 (19) and 97·5 (11), respectively; no absorption correction. Structure solution by direct methods using *MULTAN*80 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980). Anisotropic least-squares refinement (on F) of non-H positions; weights were $4F_o^2/s^2(I)$ with $s(I) = [\sigma(I)^2 + (0.06F_o)^2]^{1/2}$ and $\sigma(I)$ from counting statistics. H-atom positions were assigned from geometrical considerations assuming a C—H bond length of 1·0 Å. Isotropic thermal parameters ($1·3 \times U_c$) were also assigned and held fixed in the final stages of refinement. The final refinement cycles converged with max. $\Delta/\sigma = 0.01$; $R = 0.052$, $wR = 0.061$, $S = 1·60$, 930 observations with $I \ge 3·0\sigma(I)$, 226 variables. A final difference map showed maximum positive and negative excursions of 0·196 and 0·312 e Å^{-3}, respectively. For (II), colorless tablet from ethyl acetate, approximately $0·80 \times 0·65 \times 0·65$ mm on edge, mounted with epoxy on a glass

fiber. Cell constants from least-squares analysis of 25 reflections $[60 \le 2\theta(\text{Cu}) \le 70°]$ measured on the diffractometer. Data were collected as for (I) using a $\theta–2\theta$ scan. Systematic absences: $h00$, h odd; $00l$, $l \ne 4n$. Measured intensities: 3358, $2\theta \le 130°$, $0 \le h \le 12$, $0 \le k \le 12$, $0 \le l \le 34$; Lorentz–polarization correction; decay correction (2·3% intensity loss); absorption correction based on ψ scans (transmission coefficients: min. = 72·42, max. = 99·90%). Symmetry-equivalent reflections were averaged, $R_{\text{int}} = 0·043$ leaving 1801 unique observations. Structure solution by direct methods using *MULTAN*80. Anisotropic least-squares refinement (on F) of non-H positions; hydrogen positions were calculated from theoretical considerations assuming a C—H bond length of 1·0 Å. H atoms were assigned to atom C(1) [two half-occupancy positions based on atoms C(2A) and C(2B) and at half-occupancy for C(2A) and C(2B)]. All hydrogen positions and isotropic thermal parameters ($1·3 \times U_c$) were held fixed in the final cycles. Weights as above; convergence indicated by max. $\Delta/\sigma = 0·01$, $R = 0·065$, $wR = 0·093$, $S = 2·420$, 1576 observations with $I \ge 3\sigma(I)$, 236 variables. An extinction coefficient of the type defined by Zachariasen (1963) refined to 7·35 (2) $\times 10^{-6}$. A final difference Fourier map showed maximum positive and negative excursions of 0·254 and 0·292 e Å^{-3}. All programs from the locally modified Enraf–Nonius (1983) *SDP*; neutral-atom scattering factors from *International Tables for X-ray Crystallography* (1974), for H atoms from Stewart, Davidson & Simpson (1965).

Discussion. Figs. 1 and 2 display the structures of (I) and (II), respectively, from a common viewpoint. Positional parameters are listed in Tables 1 and 2* while Table 3 presents the principal metrical values. The structure of (I) as found in the solid state displays an *A*-ring conformation intermediate between a (1α-2β) half-chair and a 1α-sofa. Atoms C(2), C(3), C(4), C(5) and C(10) define a plane from which the largest deviation of any atom is 0·058 (6) Å. Atom C(1) is disposed 0·631 (7) Å below this plane. Alternatively, the distorted half-chair may be described by the plane defined with atoms C(3), C(4), C(5) and C(10) from which no atom deviates by more than 0·030 (6) Å. Atoms C(1) and C(2) are disposed 0·523 (7) and 0·168 (7) Å, respectively, toward the α and β faces. The *A*-ring asymmetry parameters are $\Delta C_2(1,2) = 14·2$, $\Delta C_s(1) = 12·5$, $\Delta C_s(2)$

= 32·5. The average torsion angle within the ring is 26·9°. For comparison purposes it is useful to note that the parent androst-4-ene-3,17-dione adopts a 1α-sofa A-ring conformation with $\Delta C_s(1) = 9\cdot0$ and $\Delta C_2(1,2) = 17\cdot6$ (Busetta, Comberton, Courseille & Hospital, 1972). The C(3)—C(4)—C(5)—C(10) torsion angle of $-7\cdot4\,(9)°$ in (I) shows the formally double bond to be torqued slightly from planarity; however, the distortion is only 1° larger than was observed in the androstenedione structure. The torsion angle about the C(3)—C(4) bond, which also involves sp^2 centers, is $-1\cdot6\,(8)°$; this angle was also planar in the androstenedione structure.

Substitution of the trifluoromethyl group β at C(6) induces only slight perturbations in standard B-ring geometry and conformation. The C(10)—C(5)—C(6) angle of 120·8 (5)° is comparable to the 121·1° value reported for the 6β-bromo analog (Strong, Hazel, Duax & Osawa, 1976) but wider than the 116·7° value reported for androstenedione. The B ring adopts a flattened-chair conformation with C(5) and C(8) situated 0·427 (6) and 0·684 (6) Å, respectively, below and above the plane defined by the other four ring atoms, from which none deviates by more than 0·051 (6) Å. The endocyclic bond angle at

Table 1. *Positional parameters with e.s.d.'s for* (I)

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

	x	y	z	$B_{eq}(\text{Å}^2)$
F(1)	0·4514 (5)	0·5815 (3)	0·5172 (1)	6·34 (8)
F(2)	0·5219 (5)	0·3946 (3)	0·5454 (2)	7·7 (1)
F(3)	0·2718 (5)	0·4504 (4)	0·5511 (2)	8·2 (1)
O(3)	0·8899 (5)	0·3115 (4)	0·7227 (2)	7·5 (1)
O(17)	0·3608 (5)	1·2329 (3)	0·6745 (2)	5·49 (9)
C(1)	0·8788 (6)	0·6492 (5)	0·6861 (3)	4·5 (1)
C(2)	0·9672 (6)	0·5193 (5)	0·6835 (3)	4·7 (1)
C(3)	0·8519 (6)	0·4115 (5)	0·6964 (2)	4·5 (1)
C(4)	0·6804 (6)	0·4296 (4)	0·6754 (2)	3·9 (1)
C(5)	0·6254 (6)	0·5377 (4)	0·6474 (2)	3·2 (1)
C(6)	0·4464 (6)	0·5373 (4)	0·6266 (2)	3·5 (1)
C(7)	0·3581 (6)	0·6659 (4)	0·6363 (2)	3·5 (1)
C(8)	0·4625 (6)	0·7844 (4)	0·6224 (2)	3·18 (9)
C(9)	0·6250 (5)	0·7780 (4)	0·6591 (2)	3·16 (9)
C(10)	0·7297 (6)	0·6579 (4)	0·6412 (2)	3·3 (1)
C(11)	0·7234 (6)	0·9056 (5)	0·6570 (3)	4·7 (1)
C(12)	0·6197 (6)	1·0239 (5)	0·6730 (3)	5·2 (1)
C(13)	0·4678 (6)	1·0308 (4)	0·6328 (2)	3·8 (1)
C(14)	0·3707 (5)	0·9061 (4)	0·6413 (2)	3·2 (1)
C(15)	0·2023 (7)	0·9370 (4)	0·6118 (3)	4·6 (1)
C(16)	0·1719 (6)	1·0785 (5)	0·6297 (3)	4·6 (1)
C(17)	0·3387 (6)	1·1300 (5)	0·6476 (2)	4·0 (1)
C(18)	0·5138 (7)	1·0586 (5)	0·5654 (3)	5·5 (1)
C(19)	0·7971 (7)	0·6685 (5)	0·5747 (2)	4·3 (1)
C(20)	0·4266 (7)	0·4908 (5)	0·5604 (2)	4·8 (1)

Table 2. *Positional parameters with e.s.d.'s for* (II)

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

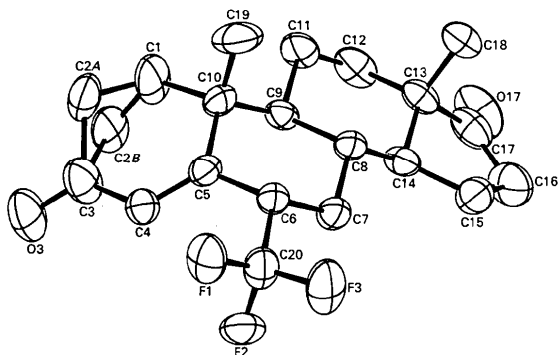|	x	y	z	$B_{eq}(\text{Å}^2)$
F(1)	0·0520 (2)	0·9657 (2)	0·45333 (8)	4·85 (5)
F(2)	0·1911 (2)	0·9066 (2)	0·49911 (9)	5·19 (5)
F(3)	0·2373 (2)	0·9496 (2)	0·43059 (9)	6·13 (6)
O(3)	−0·1706 (3)	0·7082 (3)	0·5611 (1)	6·62 (9)
O(17)	0·4876 (3)	0·1990 (3)	0·4305 (1)	7·38 (8)
C(1)	−0·0983 (4)	0·5061 (5)	0·4729 (2)	8·9 (1)
C(2B)	−0·1891 (8)	0·5731 (8)	0·4986 (4)	5·6 (2)
C(2A)	−0·1109 (8)	0·5322 (8)	0·5148 (3)	5·7 (2)
C(3)	−0·1211 (5)	0·6702 (4)	0·5267 (1)	6·2 (1)
C(4)	−0·0272 (3)	0·7388 (4)	0·5023 (1)	3·36 (7)
C(5)	0·0287 (3)	0·6967 (3)	0·4660 (1)	3·06 (7)
C(6)	0·1325 (3)	0·7644 (3)	0·4415 (1)	3·32 (7)
C(7)	0·2501 (3)	0·6898 (4)	0·4456 (1)	3·27 (7)
C(8)	0·2327 (3)	0·5618 (4)	0·4252 (1)	2·93 (7)
C(9)	0·1230 (3)	0·4953 (3)	0·4470 (1)	3·19 (7)
C(10)	0·0017 (4)	0·5705 (4)	0·4456 (1)	3·84 (8)
C(11)	0·1097 (4)	0·3639 (4)	0·4271 (1)	4·71 (9)
C(12)	0·2264 (5)	0·2873 (4)	0·4327 (1)	5·0 (1)
C(13)	0·3351 (4)	0·3541 (3)	0·4122 (1)	3·92 (8)
C(14)	0·3475 (3)	0·4829 (4)	0·4325 (1)	3·66 (8)
C(15)	0·4738 (4)	0·5289 (4)	0·4162 (2)	4·8 (1)
C(16)	0·5524 (4)	0·4107 (5)	0·4216 (2)	6·2 (1)
C(17)	0·4605 (5)	0·3046 (4)	0·4218 (1)	5·3 (1)
C(18)	0·3253 (4)	0·3551 (4)	0·3604 (1)	4·51 (9)
C(19)	−0·0466 (4)	0·5851 (4)	0·3962 (2)	5·9 (1)
C(20)	0·1524 (3)	0·8960 (3)	0·4563 (1)	3·84 (8)
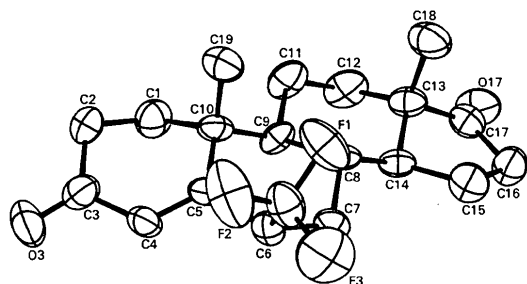
Fig. 1. *ORTEP* (Johnson, 1979) drawing of (I); non-H atoms are drawn as primary ellipses at the 50% probability level.

Fig. 2. *ORTEP* (Johson, 1979) drawing of (II); non-H atoms are drawn as primary ellipses at the 50% probability level. Position 2 of the A ring is disordered 50/50 between positions labeled C2A and C2B.

C(6) is 113·9 (5)°, identical to values of 113·7° reported for both androstenedione and the 6β-bromo analog.

The C ring adopts a chair conformation while the D-ring conformation is a 14α-envelope. Atom C(14) is disposed 0·618 (6) Å below the plane defined by the other four ring atoms, from which no atom deviates by more than 0·042 (7) Å. The asymmetry parameter, $\Delta C_s(14) = 15\cdot6$. The flattened 14α-

Table 3. *Principal bond distances* (Å) *and angles* (°)

	(I)	(II)
C(1)—C(2)	1·526 (8)	*
C(2)—C(3)	1·483 (8)	*
C(3)—C(4)	1·477 (9)	1·457 (4)
C(3)—O(3)	1·222 (7)	1·224 (4)
C(4)—C(5)	1·350 (8)	1·318 (4)
C(5)—C(6)	1·523 (8)	1·532 (4)
C(5)—C(10)	1·510 (8)	1·530 (4)
C(10)—C(1)	1·558 (9)	1·527 (5)
C(10)—C(9)	1·555 (8)	1·556 (4)
C(10)—C(19)	1·548 (8)	1·560 (4)
C(6)—C(7)	1·527 (8)	1·523 (4)
C(6)—C(20)	1·524 (8)	1·515 (4)
C(20)—F(1)	1·343 (7)	1·335 (3)
C(20)—F(2)	1·303 (8)	1·339 (4)
C(20)—F(3)	1·340 (8)	1·332 (3)
C(7)—C(8)	1·521 (7)	1·532 (4)
C(8)—C(9)	1·543 (8)	1·540 (4)
C(8)—C(14)	1·520 (8)	1·533 (4)
C(9)—C(11)	1·543 (9)	1·554 (4)
C(11)—C(12)	1·527 (9)	1·531 (5)
C(12)—C(13)	1·514 (9)	1·516 (5)
C(13)—C(14)	1·524 (8)	1·532 (4)
C(13)—C(17)	1·502 (8)	1·496 (5)
C(13)—C(18)	1·540 (8)	1·535 (3)
C(14)—C(15)	1·544 (9)	1·542 (5)
C(15)—C(16)	1·536 (8)	1·555 (5)
C(16)—C(17)	1·507 (9)	1·529 (6)
C(17)—O(17)	1·228 (6)	1·217 (4)
C(2)—C(1)—C(10)	113·2 (5)	†
C(1)—C(2)—C(3)	111·0 (5)	†
C(2)—C(3)—O(3)	124·4 (6)	†
C(2)—C(3)—C(4)	116·3 (6)	†
O(3)—C(3)—C(4)	119·4 (6)	123·1 (3)
C(3)—C(4)—C(5)	123·8 (6)	123·3 (3)
C(4)—C(5)—C(6)	116·6 (6)	124·0 (3)
C(4)—C(5)—C(10)	122·5 (5)	123·0 (3)
C(6)—C(5)—C(10)	120·8 (5)	112·9 (2)
C(5)—C(6)—C(7)	113·9 (5)	109·1 (2)
C(5)—C(6)—C(20)	112·4 (6)	115·1 (2)
C(7)—C(6)—C(20)	110·9 (5)	111·2 (2)
C(6)—C(7)—C(8)	114·4 (5)	110·5 (2)
C(7)—C(8)—C(9)	109·9 (5)	111·1 (2)
C(8)—C(9)—C(10)	111·9 (5)	113·6 (2)
C(8)—C(9)—C(11)	113·0 (5)	110·4 (2)
C(9)—C(10)—C(19)	111·7 (5)	111·4 (3)
C(5)—C(10)—C(1)	109·4 (5)	110·0 (3)
C(9)—C(11)—C(12)	113·2 (5)	112·5 (3)
C(11)—C(12)—C(13)	110·8 (5)	110·1 (3)
C(12)—C(13)—C(14)	108·2 (5)	110·6 (2)
C(12)—C(13)—C(17)	118·5 (5)	117·7 (3)
C(12)—C(13)—C(18)	111·1 (5)	110·4 (3)
C(13)—C(14)—C(15)	103·5 (5)	104·7 (2)
C(14)—C(15)—C(16)	103·6 (5)	100·9 (3)
C(15)—C(16)—C(17)	104·9 (5)	105·4 (3)
C(16)—C(17)—C(13)	109·3 (5)	109·0 (3)
C(16)—C(17)—O(17)	124·1 (6)	123·8 (4)
C(13)—C(17)—O(17)	126·3 (6)	127·1 (4)

*Position C(2) is disordered, occupying two sites. Calculated bond distances are C(1)—C(2A) = 1·280 (9), C(1)—C(2B) = 1·45 (1), C(2A)—C(3) = 1·548 (9), C(2B)—C(3) = 1·536 (8) Å.

†Bond angles involving disordered sites are C(1)—C(2A)—C(3) = 116·3 (7), C(1)—C(2B)—C(3) = 107·6 (6), C(1)—C(1)—C(2A) = 119·1 (5), C(1)—C(1)—C(2B) = 122·3 (4), C(2A)—C(3)—O(3) = 123·2 (4), C(2B)—C(3)—O(3) = 118·0 (4), C(2A)—C(3)—C(4) = 109·6 (4), C(2B)—C(3)—C(4) = 115·2 (4)°.

envelope was observed in both the androstenedione and 6β-bromoandrostenedione structures.

The A-ring bowing angle is 19·2°. The intramolecular O(3)···O(17) separation is 10·511 (6) Å.

Transannular C(19)···flourine contact distances all are greater than 3·2 Å.

The structure of (II) displays a disordered A ring with atom C(2) found in two equal-occupancy positions, labeled C(2A) and C(2B) in Fig. 2. These positions define, respectively, either a 2α- or 2β-sofa conformation for the A ring. Atoms C(1), C(3), C(4), C(5) and C(10) describe a plane from which no atom deviates. Atom C(2A) is disposed 0·499 (9) Å above this plane while atom C(2B) sits 0·562 (9) Å below the plane. The A-ring asymmetry parameters are $\Delta C_s(2A)$ = 6·5, $\Delta C_s(2B)$ = 2·4. The average torsion angle within the ring is 24·4° using angles defined by C(2A) and 24·2° using C(2B). A similar disorder was observed by Sutton & Byrn (1987) in the tetragonal form of 9α-fluorocortisol; however, observation of the 2α-sofa conformation appears to be unique in 4-ene-3-ones. As a consequence of this disorder, metrical values involving C(2) positions are inaccurate, the model having refined to a point where C(2) positions are closer than expected to C(1) and further from C(3). The C(3)—C(4)—C(5)—C(10) torsion angle of −0·7 (6)° shows planarity at the double bond, in contrast to the β-trifluoromethyl, α- and β-bromo-androstenediones as well as to the parent molecule itself. About the other A-ring sp^2 centers the torsion angle is 20·1 (4)° using C(2A) and −23·9 (4)° using atom C(2B).

In contrast both to (I) and to other 6β-substituted androstenediones, the C(10)—C(5)—C(6) angle is only 112·9 (2)° in (II). This value is consistent with the 110·9° angle reported for the 6α-bromo analog (Hazel, Strong, Duax & Osawa, 1977). In conjunction, the C(4)—C(5)—C(6) angle of 124·0 (3)° in (II) has widened by 4° over that reported for androstenedione but has not reached the 125·9° value reported for the 6α-bromo analog. The trifluoromethyl group is virtually coplanar with the A-ring double bond; the C(4)—C(5)—C(6)—C(20) torsion angle is −11·2 (5)°.

The B ring adopts a chair conformation with C(5) and C(8) situated 0·691 (3) and 0·655 (3) Å, respectively, below and above the plane defined by the other four ring atoms. The C ring also adopts a characteristic chair conformation. The D-ring conformation approximates a 14α-envelope with C(14) disposed 0·651 (3) Å below the plane defined by the other four ring atoms, from which no atom deviates by more than 0·032 (4) Å. The asymmetry parameter $\Delta C_s(14)$ = 9·2. The A-ring bowing angle is 43·9° with inclusion of all A-ring atoms in the calculation. The angle becomes 45·0° when both C(2) positions are omitted from the calculation of the least-squares plane through the A ring and becomes 40·9 or 48·8° when positions C(2A) or C(2B) are omitted, respectively. These bowing angles are near the upper limit of values observed in 4-ene-3-one structures; such

high values are consistent with other 4-ene-3-one structures in which the 'inverted' *A* ring is observed (Sutton & Byrn, 1987; Dupont, Dideberg & Campsteyn, 1972; Precigoux, Busetta, Courseille & Hospital, 1975; Duax, Cody, Griffin, Hazel & Weeks, 1978). The intramolecular $O(3) \cdots O(17)$ separation is 9·855 (5) Å.

Figs. 3(*a–c*) show overlays of (I) and both conformers of (II) with the solid-state structures of the corresponding 6-bromo analog as well as with androstenedione. The molecules were fitted to one another using the *SYBYL* (Tripos Associates Inc., 1987) molecular-modeling software package. For the fits shown, r.m.s. deviations were 0·0120 for all three structures in Fig. 3(*a*), 0·0322 in Fig. 3(*b*) and 0·0329 in Fig. 3(*c*). The preponderance of the structural results, as illustrated in these figures, indicates little perturbation of the 4-ene-3-one skeleton by the 6-trifluoromethyl substitution with the exception of *A*-ring conformation. In regard to the latter, 6β-trifluoromethyl substitution leads to a structure quite similar to both the unsubstituted parent and to another analog with a large β-oriented substituent at C(6). In contrast, 6α substitution of the trifluoromethyl group results in large *A*-ring conformational differences as compared to both the unsubstituted parent and to the 6α-bromo analog. Such differences are not induced by the large but electronically diffuse bromo substituent nor are they induced by the 6α-fluoro substituent in a related series of structures (Eggleston, Lan-Hargest & Elliott, 1990).
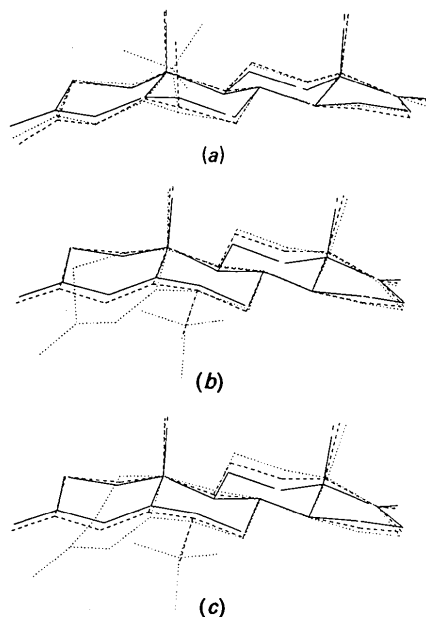

(*a*)

(*b*)

(*c*)

Fig. 3. Overlays of androstenedione (solid), and in (*a*) 6β-bromoandrostenedione (dash), 6β-trifluoromethylandrostenedione (I) (dots); (*b*) 6α-trifluoromethyl (II*A*) (dots) and 6α-bromo (dash); (*c*) 6α-trifluoromethyl (II*B*) (dots) and 6α-bromo (dash).

Table 4. *Intermolecular contacts not involving* H *atoms for* (I) *and* (II)

Distances are < 3·6 Å. For (I): 1, x, y, z; 3, $\frac{1}{2}+x$, $\frac{1}{2}-y$, $-z$; 4, $-x$, $\frac{1}{2}+y$, $\frac{1}{2}-z$. For (II): 3, $\frac{1}{2}-y$, $\frac{1}{2}+x$, $\frac{1}{4}+z$; 5, y, x, $-z$; 8, $\frac{1}{2}+x$, $\frac{1}{2}-y$, $\frac{3}{4}-z$.

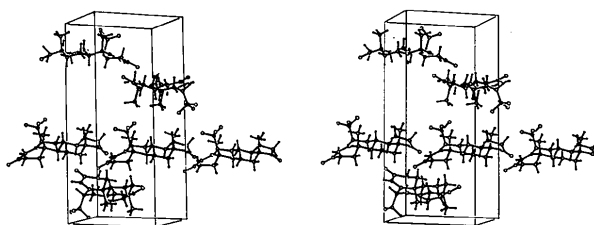|	Distance (Å)	Symmetry operator
(I)		
$F(1) \cdots C(15)$	3·471 (7)	3/011
$F(1) \cdots C(19)$	3·500 (7)	3/−1,1,1
$F(2) \cdots O(17)$	3·487 (6)	1/0,−1,0
$F(2) \cdots C(18)$	3·504 (7)	1/0,−1,0
$F(3) \cdots C(18)$	3·287 (7)	3/−111
$F(3) \cdots O(17)$	3·532 (6)	1/0,−1,0
$O(3) \cdots C(1)$	3·205 (7)	4/2,−1,1
$O(17) \cdots C(4)$	3·259 (6)	1/010
$O(17) \cdots C(6)$	3·328 (6)	1/010
(II)		
$F(1) \cdots F(1)$	3·064 (4)	5/−111
$F(1) \cdots F(2)$	3·244 (4)	5/−111
$F(2) \cdots C(1)$	3·531 (6)	5/011
$F(2) \cdots C(18)$	3·445 (3)	3/000
$F(3) \cdots C(19)$	3·293 (4)	8/010
$O(3) \cdots C(2B)$	3·488 (9)	5/−111
$O(3) \cdots C(4)$	3·578 (5)	5/−111
$O(3) \cdots C(8)$	3·586 (5)	3/000
$O(17) \cdots C(11)$	3·518 (4)	8/000
$C(3) \cdots C(3)$	3·580 (8)	5/−111

Fig. 4. Stereoview of the unit-cell packing in (I). The *b* axis is horizontal and the *c* axis vertical.
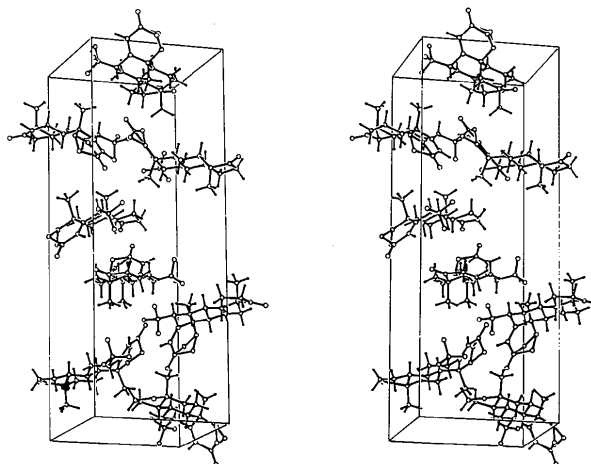

Fig. 5. Stereoview of the unit-cell packing in (II). The *a* axis is horizontal and the *c* axis vertical.

Intermolecular contacts less than 3·6 Å in length are presented for both structures in Table 4; Figs. 4 and 5 display stereo packing diagrams. While both molecules are precluded by their constitution from showing typical hydrogen-bonding interactions it is interesting to note the proximity of O(17) to both C(4) and C(6) in (I) for molecules translated along the b axis. Indeed, the H(5)···O(17) and H(6)···O(17) distances of 2·28 (4) and 2·45 (3) Å, respectively, and C(4)—H(5)···O(17) and C(6)—H(6)···O(17) angles of 160 (2) and 144 (2)°, respectively, may indicate a preferred packing arrangement based on C—H···O hydrogen bonds. In the structure of (II) no such close contacts are evident. Instead, closest contacts are of the fluorine/fluorine and fluorine/carbon type.

References

Busetta, B., Comberton, G., Courseille, C. & Hospital, M. (1972). Cryst. Struct. Commun. 1, 129–133.

Duax, W. L., Cody, V., Griffin, J. F., Hazel, J. & Weeks, C. M. (1978). J. Steriod Biochem. 9, 901–910.

Dupont, P. L., Dideberg, O. & Campsteyn, H. (1972). Acta Cryst. B28, 3023–3032.

Eggleston, D. S., Lan-Hargest, H. Y. & Elliott, J. D. (1990). Acta Cryst. Submitted.

Enraf–Nonius (1983). Structure Determination Package. Enraf–Nonius, Delft, The Netherlands.

Hazel, J. P., Strong, P. D., Duax, W. L. & Osawa, Y. (1977). Cryst. Struct. Commun. 6, 507–510.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)

Johnson, C. K. (1976). ORTEPII. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.

Lan-Hargest, H. Y., Elliott, J. D., Eggleston, D. S. & Metcalf, B. W. (1987). Tetrahedron Lett. 28, 6557–6560.

Main, P., Fiske, S. J., Hull, S. E., Lessinger, L., Germain, G., Declercq, J.-P. & Woolfson, M. M. (1980). MULTAN80. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data. Univs. of York, England, and Louvain, Belgium.

Precigoux, P. G., Busetta, B., Courseille, C. & Hospital, M. (1975). Acta Cryst. B31, 1527–1532.

Stewart, R. F., Davidson, E. R. & Simpson, W. T. (1965). J. Chem. Phys. 42, 3175–3187.

Strong, P. D., Hazel, J. P., Duax, W. L. & Osawa, Y. (1976). Cryst. Struct. Commun. 5, 275–278.

Sutton, P. A. & Byrn, S. R. (1987). J. Pharm. Sci. 76, 253–258.

Tripos Associates Inc. (1987). SYBYL. A System of Computer Programs for Molecular Modeling. Version 3.4. Tripos Associates Inc., Clayton, Missouri, USA.

Zachariasen, W. M. (1963). Acta Cryst. 16, 1139–1144.

Structure of 2-[1-(2-Thienyl)ethylideneamino]phenol

By W. Sawka-Dobrowolska, Z. Siatecki and J. M. Sobczak

Institute of Chemistry, University of Wrocław, 14 F. Joliot-Curie, 50-383 Wrocław, Poland

Abstract. $C_{12}H_{11}NOS$, $M_r = 217·7$, orthorhombic, Pnca, $a = 15·582$ (4), $b = 16·162$ (4), $c = 8·729$ (2) Å, $V = 2198·3$ Å^3, $Z = 8$, $D_m = 1·310$ (1), $D_x = 1·31$ Mg m^{-3}, $\lambda(Mo\ K\alpha) = 0·71069$ Å, $\mu = 0·26$ mm^{-1}, $F(000) = 912$, $T = 292$ K, $R = 0·044$ for 1367 observed reflexions. The thiophene and phenyl rings are planar and make a dihedral angle of 82·5 (3)°. The crystal structure is stabilized by an intermolecular H bond [2·835 (3) Å] from the phenolic OH to the imino N atom. A short intramolecular O—H···N contact of 2·866 (3) Å is also observed.

Introduction. Schiff bases are interesting ligands that give stable metal complexes. In continuing our studies of molybdenum(VI) complexes with Schiff-base ligands (Głowiak, Rucińska, Sobczak & Ziółkowski, 1987; Sobczak, Głowiak & Ziółkowski, 1990) we obtained a new crystalline monobasic bidentate Schiff base from 2-thienyl ketone and o-aminophenol.

(I)
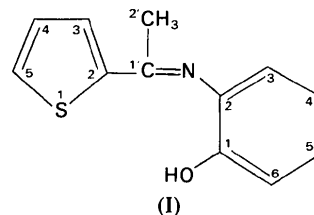
In this paper we report the synthesis and X-ray structure of 2-[1-(2-thienyl)ethylideneamino]phenol (I).

Experimental. A mixture of 0·1 mol 2-thienyl ketone, 0·1 mol o-aminophenol and 1 ml of formic acid as a catalyst in 150 ml of toluene was boiled using a Dean–Stark trap. After cooling, the title compound