Table 1. *Positional and equivalent isotropic thermal parameters* (Å²) *for non-*H *atoms with e.s.d.'s in parentheses*

$U_{eq} = (U_{11} + U_{22}\sin^2\beta + U_{33} + 2U_{13}\cos\beta)/3\sin^2\beta$.

| | $x$ | $y$ | $z$ | $U_{eq}$ |
|---|---|---|---|---|
| O(17) | 0·1705 (4) | 0·6398 (5) | 0·3349 (3) | 0·067 (1) |
| C(1) | 0·8660 (5) | 0·8343 (6) | 0·8954 (4) | 0·060 (1) |
| C(2) | 0·9486 (6) | 0·8709 (7) | 1·0287 (4) | 0·070 (2) |
| C(3) | 0·9330 (6) | 1·0089 (6) | 1·0465 (5) | 0·071 (2) |
| C(4) | 0·7413 (5) | 1·0531 (6) | 1·0055 (3) | 0·056 (1) |
| C(5) | 0·6137 (5) | 0·9875 (5) | 0·9350 (3) | 0·048 (1) |
| C(6) | 0·4156 (5) | 1·0315 (6) | 0·9122 (3) | 0·055 (1) |
| C(7) | 0·3394 (5) | 1·0162 (5) | 0·7717 (3) | 0·052 (1) |
| C(8) | 0·3691 (5) | 0·8852 (5) | 0·7243 (3) | 0·044 (1) |
| C(9) | 0·5789 (5) | 0·8522* | 0·7376 (3) | 0·043 (1) |
| C(10) | 0·6565 (5) | 0·8641 (5) | 0·8808 (3) | 0·046 (1) |
| C(11) | 0·6215 (6) | 0·7272 (5) | 0·6798 (4) | 0·054 (1) |
| C(12) | 0·5407 (5) | 0·7108 (5) | 0·5396 (3) | 0·054 (1) |
| C(13) | 0·3332 (5) | 0·7386 (5) | 0·5288 (3) | 0·047 (1) |
| C(14) | 0·3046 (5) | 0·8696 (5) | 0·5817 (3) | 0·046 (1) |
| C(15) | 0·1090 (5) | 0·9003 (6) | 0·5287 (4) | 0·057 (1) |
| C(16) | 0·0713 (5) | 0·8370 (6) | 0·4205 (4) | 0·058 (1) |
| C(17) | 0·2336 (5) | 0·7542 (5) | 0·3903 (3) | 0·052 (1) |
| C(18) | 0·2240 (6) | 0·6420 (6) | 0·6020 (4) | 0·060 (1) |
| C(20) | 0·3567 (6) | 0·8160 (6) | 0·3005 (3) | 0·056 (1) |
| C(21) | 0·4527 (8) | 0·8678 (7) | 0·2292 (4) | 0·074 (2) |

* Kept fixed during refinement.

parameters and $\Delta/\sigma = 0{\cdot}09$ (7) (av.) and 0·2 (max.) for H-atom parameters; $-0{\cdot}3 < \Delta\rho < 0{\cdot}2$ e Å$^{-3}$. Scattering factors used from *SHELX*. Final atomic parameters and equivalent isotropic thermal parameters are given in Table 1.* Bond lengths and bond angles are given in Table 2. Fig. 1 shows the molecular conformation and the atom-numbering scheme.

**Related literature.** Structural data of several other 4-ene steroids have been reviewed by Griffin, Duax & Weeks (1984). A receptor binding study of 15-ene steroids has been reported by Bergink & Kloosterboer (1985).

* Lists of structure factors, anisotropic thermal parameters, torsion angles and H-atom coordinates have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44465 (16 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Bond distances* (Å) *and bond angles* (°) *for non-*H *atoms with e.s.d.'s in parentheses*

| | | | |
|---|---|---|---|
| O(17)–C(17) | 1·439 (7) | C(9)–C(10) | 1·551 (4) |
| C(1)–C(2) | 1·517 (6) | C(9)–C(11) | 1·531 (5) |
| C(1)–C(10) | 1·533 (5) | C(11)–C(12) | 1·535 (5) |
| C(2)–C(3) | 1·53 (1) | C(12)–C(13) | 1·513 (5) |
| C(3)–C(4) | 1·492 (6) | C(13)–C(14) | 1·553 (7) |
| C(4)–C(5) | 1·342 (6) | C(13)–C(17) | 1·567 (5) |
| C(5)–C(6) | 1·502 (6) | C(13)–C(18) | 1·538 (7) |
| C(5)–C(10) | 1·501 (7) | C(14)–C(15) | 1·510 (5) |
| C(6)–C(7) | 1·526 (5) | C(15)–C(16) | 1·327 (7) |
| C(7)–C(8) | 1·534 (7) | C(16)–C(17) | 1·519 (7) |
| C(8)–C(9) | 1·542 (5) | C(17)–C(20) | 1·477 (6) |
| C(8)–C(14) | 1·523 (4) | C(20)–C(21) | 1·179 (7) |
| C(2)–C(1)–C(10) | 111·2 (4) | C(11)–C(12)–C(13) | 111·2 (3) |
| C(1)–C(2)–C(3) | 110·0 (5) | C(12)–C(13)–C(14) | 108·0 (4) |
| C(2)–C(3)–C(4) | 111·1 (4) | C(12)–C(13)–C(17) | 118·8 (3) |
| C(3)–C(4)–C(5) | 124·4 (5) | C(12)–C(13)–C(18) | 110·4 (4) |
| C(4)–C(5)–C(6) | 121·3 (5) | C(14)–C(13)–C(17) | 99·0 (4) |
| C(4)–C(5)–C(10) | 122·5 (4) | C(14)–C(13)–C(18) | 112·6 (3) |
| C(6)–C(5)–C(10) | 116·2 (4) | C(17)–C(13)–C(18) | 107·7 (3) |
| C(5)–C(6)–C(7) | 113·3 (3) | C(8)–C(14)–C(13) | 113·8 (4) |
| C(6)–C(7)–C(8) | 110·8 (4) | C(8)–C(14)–C(15) | 123·2 (3) |
| C(7)–C(8)–C(9) | 110·0 (3) | C(13)–C(14)–C(15) | 102·5 (4) |
| C(7)–C(8)–C(14) | 111·8 (4) | C(14)–C(15)–C(16) | 109·1 (4) |
| C(8)–C(9)–C(10) | 111·0 (3) | C(15)–C(16)–C(17) | 111·3 (3) |
| C(9)–C(8)–C(14) | 107·4 (3) | O(17)–C(17)–C(13) | 112·5 (4) |
| C(8)–C(9)–C(11) | 112·9 (3) | O(17)–C(17)–C(16) | 112·0 (3) |
| C(10)–C(9)–C(11) | 112·1 (3) | O(17)–C(17)–C(20) | 109·6 (3) |
| C(1)–C(10)–C(5) | 112·0 (4) | C(13)–C(17)–C(16) | 101·1 (3) |
| C(1)–C(10)–C(9) | 111·8 (3) | C(13)–C(17)–C(20) | 111·3 (3) |
| C(5)–C(10)–C(9) | 111·1 (3) | C(16)–C(17)–C(20) | 110·1 (4) |
| C(9)–C(11)–C(12) | 113·4 (4) | C(17)–C(20)–C(21) | 178·5 (7) |

We thank A. J. M. Duisenberg for collecting the X-ray data.

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# Structure of 17$\beta$-Hydroxy-11-methylene-19-nor-17$\alpha$-pregna-4,15-dien-20-yn-3-one

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**Abstract.** $C_{21}H_{24}O_2$, $M_r = 308{\cdot}42$, monoclinic, $P2_1$, $a = 8{\cdot}190$ (2), $b = 11{\cdot}705$ (2), $c = 9{\cdot}326$ (3) Å, $\beta = 98{\cdot}56$ (2)°, $V = 875{\cdot}5$ (3) Å$^3$, $Z = 2$, $D_x = 1{\cdot}170$ g cm$^{-3}$, $\lambda$(Cu $K\alpha$) = 1·54184 Å, $\mu = 5$ cm$^{-1}$, $F(000) = 332$, $T = 293$ K, $R = 0{\cdot}067$ for 1682 observations. The $A$ ring has a 1$\alpha$-sofa conformation

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Table 1. *Positional and equivalent isotropic thermal parameters* (Å²) *for non-*H *atoms with e.s.d.'s in parentheses*

$U_{eq} = (U_{11} + U_{22}\sin^2\beta + U_{33} + 2U_{13}\cos\beta)/3\sin^2\beta$.

| | $x$ | $y$ | $z$ | $U_{eq}$ |
|---|---|---|---|---|
| O(3) | −0·1730 (3) | 0·0050 (3) | 0·0092 (3) | 0·103 (1) |
| O(17) | 0·7452 (3) | 0·1092 (2) | −0·7379 (2) | 0·0663 (6) |
| C(1) | 0·1264 (5) | 0·1480 (3) | −0·1810 (3) | 0·067 (1) |
| C(2) | 0·0552 (4) | 0·1148 (4) | −0·0427 (3) | 0·071 (1) |
| C(3) | −0·0673 (4) | 0·0207 (4) | −0·0697 (3) | 0·070 (1) |
| C(4) | −0·0577 (4) | −0·0548 (4) | −0·1935 (3) | 0·065 (1) |
| C(5) | 0·0610 (3) | −0·0481 (3) | −0·2787 (3) | 0·0511 (8) |
| C(6) | 0·0672 (4) | −0·1340 (3) | −0·3971 (3) | 0·058 (1) |
| C(7) | 0·1173 (3) | −0·0815 (3) | −0·5354 (3) | 0·0528 (8) |
| C(8) | 0·2832 (3) | −0·0225 (2) | −0·4967 (3) | 0·0432 (6) |
| C(9) | 0·2699 (3) | 0·0780 (2) | −0·3893 (3) | 0·0458 (6) |
| C(10) | 0·1938 (3) | 0·0428 (3) | −0·2522 (3) | 0·0485 (8) |
| C(11) | 0·4359 (4) | 0·1393 (3) | −0·3539 (3) | 0·0512 (8) |
| C(12) | 0·5091 (4) | 0·1814 (3) | −0·4863 (3) | 0·053 (1) |
| C(13) | 0·5236 (3) | 0·0790 (2) | −0·5881 (3) | 0·0445 (6) |
| C(14) | 0·3499 (3) | 0·0268 (2) | −0·6293 (3) | 0·0433 (6) |
| C(15) | 0·3697 (3) | −0·0429 (3) | −0·7625 (3) | 0·053 (1) |
| C(16) | 0·4899 (3) | 0·0007 (3) | −0·8273 (3) | 0·056 (1) |
| C(17) | 0·5707 (3) | 0·1023 (3) | −0·7434 (3) | 0·0512 (8) |
| C(18) | 0·6503 (4) | −0·0063 (3) | −0·5116 (3) | 0·058 (1) |
| C(20) | 0·4951 (4) | 0·2087 (3) | −0·8089 (3) | 0·058 (1) |
| C(21) | 0·4322 (5) | 0·2924 (4) | −0·8632 (4) | 0·074 (1) |
| C(23) | 0·5206 (5) | 0·1510 (3) | −0·2211 (4) | 0·066 (1) |

$\{\Delta C_s[C(1)] = 3{\cdot}1\ (4)°\}$. The *B* ring has an intermediate 7α,8β-half-chair/7α-sofa conformation $\{\Delta C_2[C(7)–C(8)] = 5{\cdot}1\ (3)$ and $\Delta C_s[C(7)] = 8{\cdot}5\ (3)°\}$. The *C* ring is in the usual chair conformation and the *D* ring has a 13β-envelope conformation imposed by the $\Delta^{15}$ unsaturation $\{\Delta C_s[C(13)] = 3{\cdot}0\ (3)°\}$. Chains of hydrogen-bonded molecules are formed by O(17)→O(3′) ($x+1$, $y$, $z-1$) with O(17)···O(3′) = 2·803 (4) Å and O(17)–H···O(3′) = 163 (5)°. All other intermolecular contacts are at normal van der Waals separations.

**Experimental.** Sample obtained through the Scientific Development Group of Organon, Oss, The Netherlands. Data were collected on a triangular crystal with equilateral shape (side 0·08 mm, thickness 0·04 mm); Enraf–Nonius CAD-4 diffractometer with Ni-filtered Cu $K\alpha$ radiation; lattice parameters were refined by least-squares fitting of $2\theta$ values of 25 reflections in the range 28–34°; $\omega$–$2\theta$ scan mode, $\Delta\omega = (0{\cdot}60 + 0{\cdot}15\tan\theta)°$; 1747 independent reflections were measured, $2\theta_{max} = 140°$, $h,k,\pm l$ (max. range 9,14,11), 1682 observed reflections with $I \geq 2{\cdot}5\sigma(I)$. Standard reflections showed an intensity variation less than 2%. Lp correction applied; no corrections for absorption.

The structure was solved by direct methods with *SHELXS*86 (Sheldrick, 1986). Best *E* map of default run gave all non-H atoms. H atoms were placed at calculated positions and included in the refinement riding on their bonded atoms, except the hydroxyl, ethynyl and methylene H atoms, which were located on a difference map and refined positionally.

Table 2. *Bond distances* (Å) *and bond angles* (°) *for non-*H *atoms with e.s.d.'s in parentheses*

| | | | |
|---|---|---|---|
| O(3)–C(3) | 1·226 (4) | C(9)–C(10) | 1·548 (4) |
| O(17)–C(17) | 1·425 (4) | C(9)–C(11) | 1·529 (4) |
| C(1)–C(2) | 1·531 (4) | C(11)–C(12) | 1·522 (4) |
| C(1)–C(10) | 1·537 (5) | C(11)–C(23) | 1·323 (5) |
| C(2)–C(3) | 1·486 (6) | C(12)–C(13) | 1·539 (4) |
| C(3)–C(4) | 1·456 (5) | C(13)–C(18) | 1·534 (4) |
| C(4)–C(5) | 1·341 (4) | C(13)–C(17) | 1·564 (4) |
| C(5)–C(6) | 1·492 (4) | C(13)–C(14) | 1·543 (4) |
| C(5)–C(10) | 1·515 (4) | C(14)–C(15) | 1·505 (4) |
| C(6)–C(7) | 1·528 (4) | C(15)–C(16) | 1·328 (4) |
| C(7)–C(8) | 1·519 (4) | C(16)–C(17) | 1·517 (5) |
| C(8)–C(14) | 1·527 (4) | C(17)–C(20) | 1·479 (5) |
| C(8)–C(9) | 1·553 (4) | C(20)–C(21) | 1·183 (6) |

| | | | |
|---|---|---|---|
| C(2)–C(1)–C(10) | 111·1 (3) | C(9)–C(11)–C(23) | 125·0 (3) |
| C(1)–C(2)–C(3) | 112·3 (3) | C(9)–C(11)–C(12) | 115·1 (2) |
| O(3)–C(3)–C(4) | 120·1 (4) | C(11)–C(12)–C(13) | 108·3 (3) |
| O(3)–C(3)–C(2) | 122·0 (3) | C(17)–C(13)–C(18) | 107·1 (2) |
| C(2)–C(3)–C(4) | 117·9 (3) | C(12)–C(13)–C(18) | 109·5 (2) |
| C(3)–C(4)–C(5) | 123·6 (4) | C(14)–C(13)–C(17) | 100·8 (2) |
| C(4)–C(5)–C(10) | 120·8 (3) | C(12)–C(13)–C(17) | 118·5 (2) |
| C(4)–C(5)–C(6) | 119·8 (3) | C(14)–C(13)–C(18) | 113·0 (2) |
| C(6)–C(5)–C(10) | 119·3 (2) | C(12)–C(13)–C(14) | 107·9 (2) |
| C(5)–C(6)–C(7) | 112·6 (3) | C(8)–C(14)–C(13) | 112·3 (2) |
| C(6)–C(7)–C(8) | 109·2 (2) | C(8)–C(14)–C(15) | 123·1 (2) |
| C(7)–C(8)–C(9) | 110·5 (2) | C(13)–C(14)–C(15) | 102·0 (2) |
| C(7)–C(8)–C(14) | 113·4 (2) | C(14)–C(15)–C(16) | 109·7 (3) |
| C(9)–C(8)–C(14) | 107·1 (2) | C(15)–C(16)–C(17) | 111·6 (3) |
| C(8)–C(9)–C(10) | 113·3 (2) | O(17)–C(17)–C(16) | 114·9 (2) |
| C(8)–C(9)–C(11) | 110·3 (2) | O(17)–C(17)–C(20) | 108·9 (3) |
| C(10)–C(9)–C(11) | 113·8 (2) | C(13)–C(17)–C(16) | 100·6 (2) |
| C(5)–C(10)–C(9) | 114·9 (2) | O(17)–C(17)–C(13) | 111·1 (2) |
| C(1)–C(10)–C(5) | 109·7 (2) | C(13)–C(17)–C(20) | 112·1 (2) |
| C(1)–C(10)–C(9) | 110·5 (3) | C(16)–C(17)–C(20) | 109·1 (2) |
| C(12)–C(11)–C(23) | 119·8 (3) | C(17)–C(20)–C(21) | 178·6 (4) |

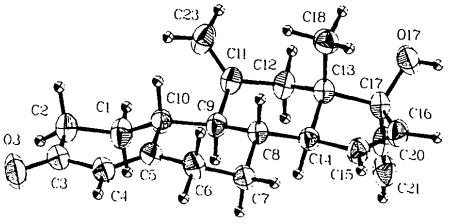


Fig. 1. Thermal-ellipsoid plot of 11β-hydroxy-19-nor-17α-pregna-4,15-dien-20-yn-3-one with ellipsoids drawn at 40% probability level.

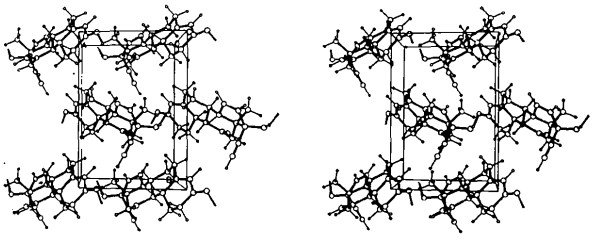

Fig. 2. Packing diagram viewed down **c**. Hydrogen bonds are indicated.

In the final cycles of two-block full-matrix least-squares refinement on *F*, using *SHELX*76 (Sheldrick, 1976), 114 and 110 parameters varied respectively; all non-H atoms refined anisotropically. The refine-

ment converged at $R = 0.047$ and $wR = 0.055$, where $w = 1/\sigma^2(F)$ and $S = 0.3$. The overall thermal parameter used for H atoms refined to $U = 0.086\ (3)$ Å$^2$. $\Delta/\sigma = 0.02$ (av.) and 0.10 (max.) for non-H-atom parameters and $\Delta/\sigma = 0.06$ (av.) and 0.13 (max.) for H-atom parameters; $-0.24 < \Delta\rho < 17$ e Å$^{-3}$. Scattering factors were taken from *SHELX*. Final atomic parameters and isotropic thermal parameters are given in Table 1.* Bond lengths and bond angles are given in Table 2. The conformation of the steroid molecule and atom-numbering scheme are shown in Fig. 1. The molecular packing and hydrogen bonding are illustrated in Fig. 2, which shows a stereoview down **c**.

**Related literature.** Structural data of 3-oxo-4-ene steroids have been reviewed by Griffin, Duax & Weeks (1984). Related steroid structures are gestodene (13-ethyl-17$\beta$-hydroxy-18,19-dinor-17$\alpha$-pregna-4,15-dien-20-yn-3-one: van Geerestein, Duisenberg, Duitz, Kanters & Kroon, 1987) and 3-ketodesogestrel (13-ethyl-17$\beta$-hydroxy-11-methylene-18,19-dinor-17$\alpha$-pregn-4-en-20-yn-3-one: van Geerestein, Kanters & Kroon, 1987).

We thank J. Kelder of Organon for supplying the crystals and B. P. van Eyck for collecting the X-ray data.

* Lists of structure factors, anisotropic thermal parameters, torsion angles and H-atom coordinates have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44466 (16 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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# Cycloaddition Product from the Reaction of Benzoquinone and 9-Bromoanthracene

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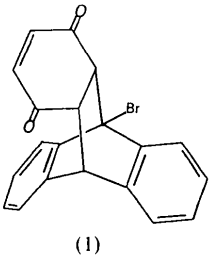
**Abstract.** 9-Bromo-4a,9,9a,10-tetrahydro-9,10-*o*-benzenoanthracene-1,4-dione, $C_{20}H_{13}BrO_2$, $M_r = 365.23$, triclinic, $P\bar{1}$, $a = 6.988\ (2)$, $b = 8.273\ (1)$, $c = 13.109\ (4)$ Å, $\alpha = 93.55\ (2)$, $\beta = 98.17\ (2)$, $\gamma = 101.49\ (2)°$, $V = 731.9\ (3)$ Å$^3$, $Z = 2$, $D_x = 1.657$ g cm$^{-3}$, $\lambda$(Mo $K\alpha$) = 0.71073 Å, $\mu = 27.85$ cm$^{-1}$, $F(000) = 368$, $T = 293$ K, $R = 0.0548$ for 2241 independent reflections. The six-membered diketone ring is in a boat conformation with the diketone moieties bent away from the adjacent phenyl ring. The ketone O(1) adjacent to the Br is bent away from the anthracene further [C(18)C(17)C(16)O(1) = $-154.9\ (6)°$] than is O(2) [C(17)C(18)C(19)O(2) = $166.8\ (6)°$]. The interplanar angles around the C(7)–C(14) direction are $123.7\ (7)°$ between C(1)C(6)C(7)C(14) and C(7)C(8)C(13)C(14), $118.5\ (7)°$ between C(1)C(6)C(7)C(14) and C(7)C(14)C(15)C(20), and $117.8\ (7)°$ for the remaining angle.

**Experimental.** Pale yellow, transparent platelet of the title compound (1) from benzene solution of a sample prepared in 1945, 0.40 × 0.57 × 0.10 mm; Nicolet $R3M/\mu$ update of $P2_1$ diffractometer; data collected in Wyckoff mode ($2\theta$ fixed, $\omega$ varied; $3.0 \le 2\theta \le 50.0°$), variable scan rate (4–29.3° min$^{-1}$), graphite-mono-




(1)

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