

1537 reflections  
153 parameters  
All H-atom parameters refined  
 $w = 1/[\sigma^2(F) + 0.001F^2]$

Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV, Table 2.3.1)

Sheldrick, G. M. (1990). *SHELXTL-Plus*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.  
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Zhang, J.-Z., Xing, L.-S. & Wang, Y.-L. (1982). *Tien-chin I Yao*, **10**, 617–618.

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters ( $\text{\AA}^2$ )

$$U_{eq} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j$$

	x	y	z	$U_{eq}$
O	0.3725 (2)	0.6828 (2)	0.1022 (1)	0.051 (1)
N(1)	0.4777 (2)	0.2584 (2)	0.0950 (1)	0.039 (1)
N(2)	-0.1524 (2)	0.5030 (3)	0.1916 (1)	0.053 (1)
C(1)	0.6379 (3)	0.3119 (2)	0.0595 (1)	0.040 (1)
C(2)	0.7755 (3)	0.0686 (3)	0.0460 (1)	0.039 (1)
C(3)	0.9338 (3)	0.1218 (3)	0.0077 (1)	0.038 (1)
C(4)	0.3571 (2)	0.4528 (2)	0.1139 (1)	0.036 (1)
C(5)	0.2004 (2)	0.3792 (2)	0.1505 (1)	0.036 (1)
C(6)	0.2505 (3)	0.1635 (3)	0.1768 (1)	0.043 (1)
C(7)	0.0975 (3)	0.1217 (3)	0.2108 (1)	0.050 (1)
C(8)	-0.0978 (3)	0.2956 (3)	0.2168 (1)	0.052 (1)
C(9)	-0.0035 (3)	0.5418 (3)	0.1592 (1)	0.043 (1)

Table 2. Selected geometric parameters ( $\text{\AA}$ ,  $^\circ$ )

O—C(4)	1.232 (2)	C(3)—C(3')	1.517 (3)
N(1)—C(1)	1.460 (2)	C(4)—C(5)	1.498 (2)
N(1)—C(4)	1.334 (2)	C(5)—C(6)	1.381 (2)
N(2)—C(8)	1.331 (2)	C(5)—C(9)	1.392 (2)
N(2)—C(9)	1.334 (2)	C(6)—C(7)	1.386 (2)
C(1)—C(2)	1.509 (2)	C(7)—C(8)	1.375 (2)
C(2)—C(3)	1.523 (2)		
C(1)—N(1)—C(4)	120.7 (1)	C(4)—C(5)—C(6)	123.9 (1)
C(8)—N(2)—C(9)	116.6 (1)	C(4)—C(5)—C(9)	118.0 (1)
N(1)—C(1)—C(2)	111.7 (1)	C(6)—C(5)—C(9)	118.1 (1)
C(1)—C(2)—C(3)	111.7 (1)	C(5)—C(6)—C(7)	118.5 (1)
C(2)—C(3)—C(3')	112.9 (1)	C(6)—C(7)—C(8)	118.9 (1)
O—C(4)—N(1)	122.2 (1)	N(2)—C(8)—C(7)	124.0 (1)
O—C(4)—C(5)	120.9 (1)	N(2)—C(9)—C(5)	123.9 (1)
N(1)—C(4)—C(5)	116.9 (1)		

Symmetry code: (i)  $2 - x, -y, -z$ .

The structure was solved and refined using *SHELXTL-Plus* (Sheldrick, 1990). All calculations were carried out using *SHELXTL-Plus* and the figure was produced with *PLATON* (Spek, 1990).

This work was supported by the National Natural Science Foundation of China.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, complete geometry and torsion angles have been deposited with the IUCr (Reference: TA1081). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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## 17 $\alpha$ -Ethynyl-19-nor-3-oxo-4-androsten-17 $\beta$ -yl Acetate (Norethindrone Acetate)

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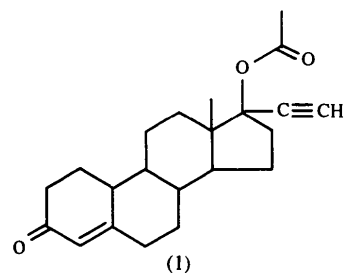
(Received 4 December 1995; accepted 16 February 1996)

## Abstract

The steroid skeleton of the title compound,  $C_{22}H_{28}O_3$ , is almost identical to the parent molecule norethindrone. The ethynyl residue donates a  $C\equiv C-H\cdots O=C$  hydrogen-bond interaction, with an  $H\cdots O$  separation of 2.18  $\text{\AA}$ .

## Comment

17 $\alpha$ -Ethynyl steroids are widely used as constituents of contraceptive agents and numerous crystal structures have been determined (*e.g.* van Geerestein, 1988). The structure of the parent molecule of the title compound, norethindrone, was reported by Moron, Lepicard & Delettre (1976). Recently, Lutz, van der Maas & Kanters (1994) pointed out that ethynyl steroids may serve as a model to study  $C-H\cdots O$  interactions donated by the ethynyl residue  $C\equiv C-H$ . The latter is known to be one of the most acidic  $C-H$  groups and therefore one of the strongest  $C-H$  hydrogen-bond donors (see Desiraju, 1991; Steiner, 1994a). In this context, the crystal structure of the title compound (1) was determined.



The molecular conformation of the steroid skeleton (Fig. 1) is almost identical with that of norethindrone (Moron, Lepicard & Delettre, 1976), and therefore

need not be discussed here further. By far the strongest hydrogen-bond donor in (1) is the ethynyl residue and the second strongest is C(4)—H (as a result of the  $sp^2$  hybridization). All other C—H groups are of lesser acidity and therefore have only poor donor strength (see Pedireddi & Desiraju, 1992). Two strong acceptors compete for these donors, C(3)=O(3) and C(22)=O(22), whereas C—O(17)—C is a weaker acceptor (Steiner, 1994b) and is at the same time sterically poorly accessible. In the crystal structure, molecules are arranged in a head-to-tail fashion (Fig. 2). As expected, C≡C—H donates the shortest C—H...O hydrogen bond, C(21)—H...O(3), which has an H...O separation of only 2.18 Å [C...O = 3.10 (1) Å; Table 3]. C(4)—H donates a longer C—H...O interaction to O(22).

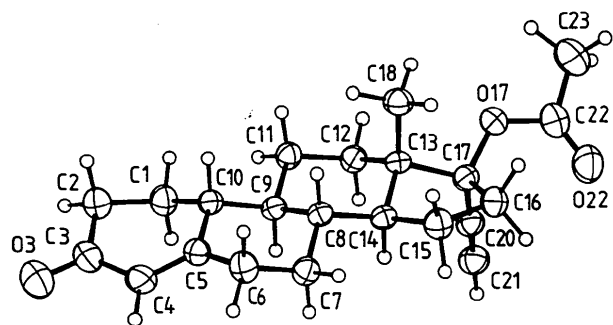


Fig. 1. Molecular structure and atomic numbering scheme (30% probability ellipsoids).

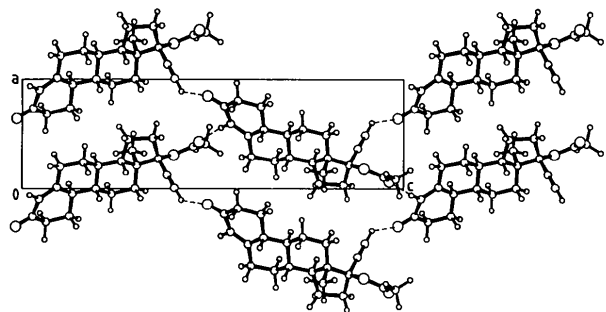


Fig. 2. Section of the crystal packing around  $y/b = 0.5$ , projection is on the  $ac$  plane. Hydrogen bonds are shown as dashed lines.

Hydrogen-bond interactions of terminal alkynes can be very well observed in the IR spectrum. In the present case, some relevant IR stretching frequencies measured from crystals and 'free' molecules in non-polar solution are listed in Table 4. A very pronounced effect is observed for the interaction  $\equiv\text{C}(21)\text{—H}\cdots\text{O}(3)=\text{C}(3)$ , which causes spectral downshifts of  $\nu_{\text{CH}}$  by  $-71\text{ cm}^{-1}$  and of  $\nu_{\text{CO}}$  by  $-10.2\text{ cm}^{-1}$ . The much weaker interaction C(4)—H...O(22) hardly reflects in the IR spectrum.

## Experimental

The title compound is commercially available (Sigma) and was recrystallized from methanol.

## Crystal data

C<sub>22</sub>H<sub>28</sub>O<sub>3</sub>  
 $M_r = 340.5$   
 Orthorhombic  
 $P2_12_12_1$   
 $a = 6.8302$  (8) Å  
 $b = 12.164$  (1) Å  
 $c = 23.846$  (4) Å  
 $V = 1981.2$  (4) Å<sup>3</sup>  
 $Z = 4$   
 $D_x = 1.14\text{ Mg m}^{-3}$   
 $D_m$  not measured

Cu  $K\alpha$  radiation  
 $\lambda = 1.54184$  Å  
 Cell parameters from 25 reflections  
 $\theta = 7.5\text{--}30.4^\circ$   
 $\mu = 0.587\text{ mm}^{-1}$   
 Room temperature  
 Plate  
 $0.5 \times 0.3 \times 0.04\text{ mm}$   
 Colourless

## Data collection

Enraf-Nonius Turbo CAD-4 diffractometer  
 $\omega/2\theta$  scans  
 Absorption correction: none  
 1765 measured reflections  
 1704 independent reflections  
 1437 observed reflections [ $I > 2\sigma(I)$ ]

$R_{\text{int}} = 0.010$   
 $\theta_{\text{max}} = 59.8^\circ$   
 $h = -7 \rightarrow 0$   
 $k = 0 \rightarrow 13$   
 $l = -26 \rightarrow 1$   
 3 standard reflections monitored every 200 reflections  
 intensity decay: 1.0%

## Refinement

Refinement on  $F^2$   
 $R(F) = 0.059$   
 $wR(F^2) = 0.156$   
 $S = 1.09$   
 1704 reflections  
 255 parameters  
 H atoms see text  
 $w = 1/[\sigma^2(F^2) + (0.0796P)^2 + 1.1716P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\text{max}} < 0.001$   
 $\Delta\rho_{\text{max}} = 0.14\text{ e \AA}^{-3}$   
 $\Delta\rho_{\text{min}} = -0.16\text{ e \AA}^{-3}$   
 Extinction correction: none  
 Atomic scattering factors from SHELLXL93 (Sheldrick, 1993)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å<sup>2</sup>)

$$U_{\text{eq}} = (1/3)\sum_i\sum_j U_{ij}a_i^*a_j^*a_i\cdot a_j.$$

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{eq}}$
O(3)	0.8519 (8)	0.6463 (4)	0.4845 (2)	0.119 (2)
O(17)	0.1844 (6)	0.7420 (3)	0.8955 (1)	0.066 (1)
C(1)	0.7584 (9)	0.7448 (5)	0.6246 (2)	0.070 (2)
C(2)	0.8118 (9)	0.7629 (5)	0.5633 (2)	0.073 (2)
C(3)	0.7622 (9)	0.6662 (5)	0.5283 (2)	0.074 (2)
C(4)	0.5980 (10)	0.5982 (4)	0.5451 (2)	0.076 (2)
C(5)	0.4884 (8)	0.6219 (4)	0.5905 (2)	0.058 (1)
C(6)	0.2964 (9)	0.5658 (5)	0.5992 (2)	0.072 (2)
C(7)	0.2558 (9)	0.5362 (4)	0.6604 (2)	0.065 (1)
C(8)	0.2861 (7)	0.6357 (3)	0.6989 (2)	0.049 (1)
C(9)	0.4998 (8)	0.6767 (3)	0.6928 (2)	0.050 (1)
C(10)	0.5459 (8)	0.7107 (4)	0.6318 (2)	0.055 (1)
C(11)	0.5488 (8)	0.7697 (4)	0.7343 (2)	0.058 (1)
C(12)	0.4961 (8)	0.7400 (4)	0.7953 (2)	0.059 (1)
C(13)	0.2823 (7)	0.7047 (3)	0.7995 (2)	0.048 (1)
C(14)	0.2456 (7)	0.6074 (3)	0.7602 (2)	0.050 (1)
C(15)	0.0456 (9)	0.5643 (5)	0.7768 (2)	0.070 (2)
C(16)	0.0322 (8)	0.5867 (5)	0.8414 (2)	0.066 (1)
C(17)	0.2196 (8)	0.6520 (4)	0.8564 (2)	0.054 (1)
C(18)	0.1453 (9)	0.8021 (4)	0.7877 (2)	0.070 (2)
C(20)	0.3704 (9)	0.5805 (4)	0.8796 (2)	0.059 (1)
C(21)	0.4927 (10)	0.5237 (4)	0.8987 (2)	0.069 (2)
C(22)	0.1072 (10)	0.7199 (6)	0.9466 (2)	0.083 (2)
O(22)	0.0641 (8)	0.6288 (4)	0.9617 (2)	0.107 (2)
C(23)	0.0855 (14)	0.8254 (6)	0.9789 (3)	0.114 (3)

Table 2. Selected geometric parameters ( $\text{\AA}$ ,  $^\circ$ )

O(3)—C(3)	1.234 (6)	C(9)—C(11)	1.541 (6)
O(17)—C(22)	1.355 (7)	C(9)—C(10)	1.545 (6)
O(17)—C(17)	1.458 (5)	C(11)—C(12)	1.540 (6)
C(1)—C(10)	1.519 (8)	C(12)—C(13)	1.526 (7)
C(1)—C(2)	1.524 (7)	C(13)—C(14)	1.530 (6)
C(2)—C(3)	1.482 (7)	C(13)—C(18)	1.536 (6)
C(3)—C(4)	1.450 (8)	C(13)—C(17)	1.561 (6)
C(4)—C(5)	1.348 (7)	C(14)—C(15)	1.515 (8)
C(5)—C(6)	1.493 (8)	C(15)—C(16)	1.567 (7)
C(5)—C(10)	1.513 (6)	C(16)—C(17)	1.549 (7)
C(6)—C(7)	1.528 (7)	C(17)—C(20)	1.457 (8)
C(7)—C(8)	1.532 (6)	C(20)—C(21)	1.176 (7)
C(8)—C(14)	1.526 (6)	O(22)—C(22)	1.202 (7)
C(8)—C(9)	1.550 (7)	C(22)—C(23)	1.503 (8)
C(22)—O(17)—C(17)	119.4 (4)	C(13)—C(12)—C(11)	110.6 (4)
C(10)—C(1)—C(2)	112.1 (5)	C(12)—C(13)—C(14)	109.5 (4)
C(3)—C(2)—C(1)	111.7 (5)	C(12)—C(13)—C(18)	110.7 (4)
O(3)—C(3)—C(4)	120.4 (6)	C(14)—C(13)—C(18)	112.7 (4)
O(3)—C(3)—C(2)	121.2 (6)	C(12)—C(13)—C(17)	115.8 (4)
C(4)—C(3)—C(2)	118.3 (5)	C(14)—C(13)—C(17)	99.8 (3)
C(5)—C(4)—C(3)	122.0 (5)	C(18)—C(13)—C(17)	107.9 (4)
C(4)—C(5)—C(6)	120.1 (5)	C(15)—C(14)—C(8)	119.4 (4)
C(4)—C(5)—C(10)	122.1 (5)	C(15)—C(14)—C(13)	104.8 (4)
C(6)—C(5)—C(10)	117.6 (4)	C(8)—C(14)—C(13)	112.4 (3)
C(5)—C(6)—C(7)	113.6 (4)	C(14)—C(15)—C(16)	104.4 (4)
C(6)—C(7)—C(8)	111.2 (4)	C(17)—C(16)—C(15)	105.6 (4)
C(14)—C(8)—C(7)	111.8 (4)	C(20)—C(17)—O(17)	108.7 (4)
C(14)—C(8)—C(9)	109.5 (4)	C(20)—C(17)—C(16)	111.5 (4)
C(7)—C(8)—C(9)	109.0 (4)	O(17)—C(17)—C(16)	113.4 (4)
C(11)—C(9)—C(10)	111.4 (4)	C(20)—C(17)—C(13)	112.4 (4)
C(11)—C(9)—C(8)	112.4 (4)	O(17)—C(17)—C(13)	107.1 (3)
C(10)—C(9)—C(8)	111.5 (4)	C(16)—C(17)—C(13)	103.6 (4)
C(5)—C(10)—C(1)	111.7 (4)	C(21)—C(20)—C(17)	179.4 (5)
C(5)—C(10)—C(9)	111.6 (4)	O(22)—C(22)—O(17)	123.2 (5)
C(1)—C(10)—C(9)	111.9 (4)	O(22)—C(22)—C(23)	127.6 (6)
C(12)—C(11)—C(9)	112.5 (4)	O(17)—C(22)—C(23)	109.2 (6)
C(13)—C(17)—O(17)—C(22)	172.9 (5)		
C(16)—C(17)—O(17)—C(22)	59.2 (6)		
C(17)—O(17)—C(22)—O(22)	-0.6 (9)		
C(17)—O(17)—C(22)—C(23)	179.9 (5)		

Table 3. C—H...O hydrogen-bond parameters ( $\text{\AA}$ ,  $^\circ$ )

As H-atom positions are theoretical (C—H 1.09  $\text{\AA}$ ), no e.s.d.'s are given for parameters involving H atoms.

C—H...O	H...O	C...O	C—H...O	H...O=C
C21—H...O3 <sup>i</sup>	2.18	3.097 (7)	140	145
C4—H...O22 <sup>ii</sup>	2.49	3.578 (7)	172	161

Symmetry codes: (i)  $\frac{1}{2} - x, 1 - y, z + \frac{3}{2}$ ; (ii)  $\frac{1}{2} - x, 1 - y, z - \frac{3}{2}$ .

Table 4. Selected IR stretching frequencies (FTIR;  $\text{cm}^{-1}$ )

	In CCL <sub>4</sub>	Crystal	$\Delta\nu$
$\nu_{\text{C-H}}$	3309.5	3238.5	-71.0
$\nu_{\text{C=O}}$ (C3=O3) <sup>a</sup>	1678.4	1668.2	-10.2
$\nu_{\text{C=O}}$ (C22=O22) <sup>a</sup>	1751.5	1751.1	-0.4

<sup>a</sup> Assignment of the two  $\nu_{\text{C=O}}$  bands is unambiguous since the  $\nu_{\text{CO}}$  value for the ester C22=O22 must be at appreciably higher wavenumbers than that of the ketone C3=O3.

H atoms were treated using a riding model (SHELXL93; Sheldrick, 1993) with C—H = 1.09  $\text{\AA}$ .

Data collection: CAD-4 Software (Enraf-Nonius, 1989). Cell refinement: CAD-4 Software. Data reduction: CAD-4 Software. Program(s) used to solve structure: SHELXS86 (Sheldrick, 1985). Program(s) used to refine structure: SHELXL93 (Sheldrick, 1993). Molecular graphics: ORTEPII (Johnson, 1976). Software used to prepare material for publication: SHELXL93.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: KA1177). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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## Triphenylpropargylphosphonium Bromide

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## Abstract

The asymmetric crystal unit of the title compound, C<sub>21</sub>H<sub>18</sub>P<sup>+</sup>.Br<sup>-</sup>, contains two formula units of similar geometry. The alkynyl residues of both independent cations donate hydrogen bonds to bromide ions with