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Structures of Some New D-Secoestrone Derivatives

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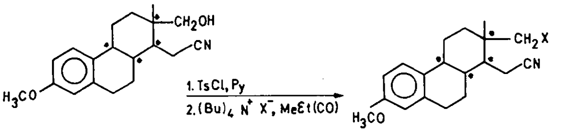
Abstract. $C_{19}H_{24}NOX$ (X = Cl, Br, I; the three compounds are isostructural), monoclinic, $P2_1$, $Z = 2$, λ(Mo $K\alpha$) = 0.71069 Å. 17-Chloro-3-methoxy-16,17-secoestra-1,3,5(10)-triene-16-nitrile (1), M_r = 371.860, a = 7.768 (2), b = 14.590 (5), c = 7.647 (2) Å, β = 96.16 (3)°, V = 861.7 (6) Å^3, D_x = 1.225 g cm^{-3}, μ = 1.83 cm^{-1}, F(000) = 340, T_c = 391–392 K, R = 0.040 for 1098 observed reflections. 17-Bromo-3-methoxy-16,17-secoestra-1,3,5(10)-triene-16-nitrile (2), M_r = 362.316, a = 7.774 (2), b = 14.615 (7), c = 7.719 (3) Å, β = 96.50 (2)°, V = 871.4 (9) Å^3, D_x = 1.380 g cm^{-3}, μ = 22.89 cm^{-1}, F(000) = 376, T_c = 402–403 K, R = 0.035 for 1136 observed reflections. 17-Iodo-3-methoxy-16,17-secoestra-1,3,5(10)-triene-16-nitrile (3), M_r = 409.311, a = 7.832 (3), b = 14.668 (8), c = 7.872 (3) Å, β = 97.05 (2)°, V = 897 (1) Å^3, D_x = 1.514 g cm^{-3}, μ = 16.49 cm^{-1}, F(000) = 412, T_c = 407–408 K, R = 0.049 for 1659 observed reflections. These three new D-secoestrone derivatives have been synthesized and submitted to a biological screening of their possible antiestrogenic activities.

Introduction. In an earlier paper (Petrović, Pejanović, Miljković & Hranisavljević, 1990) we proved that some newly synthesized D-secoestrone derivatives completely lack estrogen activity. Though this fact was already established for some other D-seco- and D-heteroestrone derivatives (Baran, 1967), there is no evidence in the literature about their structure–biological activity relationship. On the other hand, for some natural estrogen derivatives such relationships have been firmly established (Segaloff, Gabbard, Flores, Borne, Baker, Duax, Strong & Rohrer, 1980).

Therefore we have undertaken X-ray structure determinations of selected D-secoestrone derivatives, with an aim to explain their biological behaviour. The D-secoestrone derivatives tested were obtained according to the scheme below (Petrović *et al.*, 1990).



(1) X = Cl
(2) X = Br
(3) X = I

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Experimental. All three compounds crystallize as colourless transparent prisms. Intensities were collected on a Philips PW1100 diffractometer with graphite-monochromated Mo $K\alpha$ radiation using ω scans for compound (1) and ω–2θ scans for compounds (2) and (3) in the range $2 < \theta < 28°$. The reflections were monitored every 2 h and no observable changes in their intensities were observed. Data were corrected for Lp but not for absorption. The systematic absences correspond to those of the monoclinic space group $P2_1$, $Z = 2$. The refined lattice parameters were obtained by a least-squares procedure from the setting angles of 18 reflections with $6 < \theta < 11°$ for all three compounds.

The phase problem for the Br compound (2) was solved by Patterson methods using *SHELXS*86 (Sheldrick, 1986). Because all three compounds are isostructural, the structures of the remaining two compounds, (1) and (3), were solved by applying the atomic coordinates of the first compound. The positions of the H atoms were generated from assumed geometry and refined as 'riding groups'. All non-H atoms were treated anisotropically. For H atoms the overall isotropic temperature factors for different CH types were refined. $\sum w(\Delta F^2)$ was minimized, with $w = k/[\sigma^2(F_o) + gF_o^2]$, $\sigma(F)$ obtained from counting statistics, k and g optimized in the least-squares procedure. All calculations were performed on a PC/AT computer using *SHELX*76 (Sheldrick, 1976) and *CSU* (Vicković, 1988) programs. The atomic scattering factors are as in *SHELX*76; for the I atom the scattering factors were taken from *International Tables for X-ray Crystallography* (1962, Vol. III).

17-Chloro-3-methoxy-16,17-secoestra-1,3,5(10)-triene-16-nitrile (1): crystal dimensions 0.255 × 0.720 × 0.045 mm; h −10 to 10, k 0 to 18, l 0 to 9; standard reflections $\bar{3}31$, $2\bar{5}\bar{2}$, $2\bar{4}2$; 1213 reflections collected, 1098 observed with $F_o > 6\sigma(F_o)$; 202 parameters refined, R(based on F) = 0.040, $wR = 0.043$, $S = 0.53$, $k = 1.32$, $g = 0.0001$; maximum and minimum peak heights in final $\Delta\rho$ map 0.17 and −0.21 e Å^{-3}; $(\Delta/\sigma)_{\max} = 0.002$.

17-Bromo-3-methoxy-16,17-secoestra-1,3,5(10)-triene-16-nitrile (2): crystal dimensions 0.275 × 0.300 × 0.210 mm; h 10 to −10, k 0 to 18, l 0 to 10; standard reflections $\bar{3}31$, $2\bar{5}\bar{2}$, $2\bar{4}2$; 1695 reflections collected, 1136 observed with $F_o > 6\sigma(F_o)$; 202 parameters refined, R(based on F) = 0.035, wR = 0.036, $S = 0.82$, $k = 1.033$, $g = 0.0002$; maximum and minimum peak heights in final $\Delta\rho$ map 0.39 and −0.24 e Å^{-3}; $(\Delta/\sigma)_{\max} = 0.002$.

17-Iodo-3-methoxy-16,17-secoestra-1,3,5(10)-triene-16-nitrile (3): crystal dimensions 0.060 × 0.368 × 0.390 mm; h −10 to 10, k 0 to 19, l 0 to 10; standard reflections $\bar{1}71$, $0\bar{5}2$, $\bar{1}\bar{8}1$; 1909 reflections collected, 1695 observed with $F_o > 6\sigma(F_o)$; 202 parameters refined, R(based on F) = 0.049, $wR = 0.054$, $S = 1.20$, $k = 1.830$, $g = 0.0008$; maximum and minimum peak heights in final $\Delta\rho$ map 0.80 and −0.72 e Å^{-3}; $(\Delta/\sigma)_{\max} = 0.064$.

Table 1. *Fractional atomic coordinates* (× 10^4) *and equivalent isotropic temperature factors* (Å^2 × 10^3)

$$U_{eq} = (1/3)[(U_{11} + U_{33})\sin^{-2}\beta + U_{22} + 2U_{13}\sin^{-2}\beta\cos\beta].$$

(1)	x	y	z	U_{eq}
Cl	8678 (2)	0*	8866 (2)	76 (1)
O	1329 (7)	2649 (4)	−2118 (5)	74 (1)
N	1680 (8)	−1810 (5)	6915 (8)	83 (2)
C(1)	4759 (8)	1568 (4)	735 (7)	48 (1)
C(2)	3876 (8)	2041 (4)	−638 (7)	52 (1)
C(3)	2105 (8)	2149 (4)	−708 (7)	50 (2)
C(4)	1224 (8)	1785 (4)	598 (7)	49 (1)
C(5)	2111 (7)	1302 (4)	1999 (7)	43 (1)
C(6)	1088 (7)	949 (4)	3440 (7)	49 (1)
C(7)	2208 (6)	771 (4)	5161 (7)	45 (1)
C(8)	3779 (6)	185 (4)	4832 (5)	37 (1)
C(9)	4919 (6)	704 (4)	3642 (6)	39 (1)
C(10)	3889 (7)	1176 (4)	2083 (6)	39 (1)
C(11)	6358 (6)	69 (5)	3127 (6)	45 (1)
C(12)	7464 (7)	−264 (4)	4767 (7)	47 (1)
C(13)	6421 (7)	−745 (4)	6123 (7)	44 (1)
C(14)	4906 (6)	−114 (4)	6524 (6)	36 (1)
C(15)	3817 (7)	−497 (4)	7959 (6)	45 (1)
C(16)	2642 (8)	−1248 (5)	7360 (8)	53 (2)
C(17)	7653 (8)	−967 (4)	7746 (8)	57 (2)
C(18)	5799 (8)	−1697 (4)	5375 (9)	63 (2)
C(19)	−484 (10)	2768 (6)	−2264 (9)	92 (2)
(2)				
Br	8791 (1)	0*	8889 (1)	64 (1)
0	1243 (9)	2655 (5)	−2089 (8)	67 (2)
N	1710 (10)	−1819 (6)	6863 (12)	78 (3)
C(1)	4691 (10)	1581 (6)	739 (9)	43 (2)
C(2)	3793 (11)	2048 (6)	−622 (10)	52 (2)
C(3)	2019 (11)	2175 (6)	−684 (10)	46 (2)
C(4)	1178 (10)	1827 (6)	639 (9)	46 (2)
C(5)	2062 (9)	1348 (6)	2047 (9)	38 (2)
C(6)	1053 (9)	1000 (6)	3474 (9)	47 (2)
C(7)	2219 (9)	810 (6)	5171 (8)	39 (2)
C(8)	3770 (8)	206 (5)	4791 (8)	30 (2)
C(9)	4900 (9)	732 (5)	3618 (8)	35 (2)
C(10)	3850 (9)	1215 (5)	2085 (9)	36 (2)
C(11)	6295 (8)	85 (10)	3073 (8)	45 (2)
C(12)	7430 (9)	−258 (5)	4677 (9)	40 (2)
C(13)	6402 (9)	−755 (5)	5983 (10)	38 (2)
C(14)	4903 (8)	−107 (7)	6451 (8)	33 (2)
C(15)	3843 (9)	−509 (6)	7875 (9)	40 (2)
C(16)	2639 (10)	−1241 (7)	7291 (11)	50 (2)
C(17)	7623 (10)	−1025 (6)	7582 (10)	46 (2)
C(18)	5745 (11)	−1682 (6)	5214 (12)	57 (2)
C(19)	−562 (14)	2794 (8)	−2219 (13)	87 (3)
(3)				
I	8907 (1)	0*	8905 (1)	59 (1)
O	1100 (13)	2690 (7)	−2003 (11)	75 (3)
N	1755 (16)	−1796 (9)	6696 (20)	87 (4)
C(1)	4600 (15)	1645 (9)	762 (14)	52 (3)
C(2)	3659 (18)	2118 (10)	−578 (14)	62 (3)
C(3)	1916 (17)	2238 (9)	−619 (13)	56 (3)
C(4)	1088 (16)	1926 (9)	722 (14)	53 (3)
C(5)	2051 (13)	1441 (8)	2107 (12)	41 (2)
C(6)	1059 (12)	1096 (9)	3534 (13)	46 (3)
C(7)	2276 (12)	877 (8)	5156 (12)	41 (2)
C(8)	3748 (11)	270 (6)	4722 (11)	32 (2)
C(9)	4890 (12)	786 (7)	3589 (12)	37 (2)
C(10)	3796 (13)	1299 (8)	2117 (12)	41 (2)
C(11)	6255 (13)	192 (9)	3016 (12)	45 (3)
C(12)	7380 (12)	−211 (7)	4518 (13)	43 (3)
C(13)	6350 (12)	−730 (7)	5789 (13)	39 (2)
C(14)	4924 (11)	−96 (11)	6316 (11)	36 (2)
C(15)	3905 (13)	−514 (7)	7726 (13)	40 (2)
C(16)	2690 (15)	−1231 (9)	7126 (17)	56 (3)
C(17)	7608 (14)	−1046 (8)	7318 (13)	46 (2)
C(18)	5647 (15)	−1609 (9)	4934 (18)	56 (3)
C(19)	−712 (21)	2831 (13)	−2104 (20)	89 (5)

* Coordinates fixed to define origin for structures with non-centrosymmetric space groups.

Discussion. A perspective view of the bromide derivative (2), computed from the final atomic coordinates listed in Table 1,* is depicted in Fig. 1. The molecules of the other two compounds are practically the same. Since the starting material was synthesized from natural estrone, the absolute stereochemistry of which is known (Fieser & Fieser, 1967), the X-ray structures of (1), (2) and (3) are described with the appropriate enantiomers. The bond lengths, angles and relevant torsion angles are given in Table 2.

The bond distances, including *X*—C (*X* = Cl, Br and I), are in good agreement with the literature. Apart from *X*—C bonds, the corresponding bond distances as well as bond angles and torsion angles in (1), (2) and (3) agree within experimental error. Accordingly, the conformation of ring *B*, the only flexible ring in 1,3,5(10)-estratriene steroids (Duax, Weeks & Rohrer, 1976) is the same in all three molecules.

Ring-puckering coordinates (Cremer & Pople, 1975), asymmetry parameters (Duax *et al.*, 1976) and asymmetry factors (Kálmán, Czugler & Simon, 1982), listed in Table 3, define the conformations of *B* and *C* rings in all three compounds. The aromatic *A* ring is essentially planar. The *B* ring exhibits a $7\alpha,8\beta$-half-chair conformation distorted with considerable magnitude towards 7α-envelope (sofa), while the saturated *C* ring adopts an almost ideal chair conformation. The 3-methoxy group lies in the plane of the benzene ring. The C(17)—*X* moiety is in an α-equatorial position, while C(15)—C(16)≡N is β-equatorial. The twist along the principal axis of the steroid molecule, defined by the non-bonded torsion angle C(1)—C(10)···C(13)—C(18) of −99.3 (5), −97.1 (7) and −93.6 (1)° for (1), (2) and (3), respectively, is practically negligible.

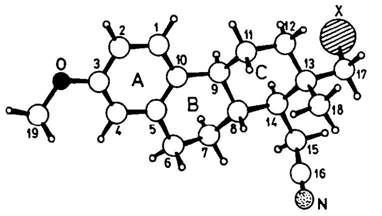

Fig. 1. A perspective view of the bromo derivative (2). The C atoms are numbered. *X* = Br. Br···O = 10.490 (7) Å [*X*···O = 10.383 (8) and 10.668 (9) Å for *X* = Cl and I, respectively].

Table 2. *Bond distances* (Å), *bond angles* (°) *and selected torsion angles* (°) *for* (1), (2) *and* (3)

	(1)(*X* = Cl)	(2)(*X* = Br)	(3)(*X* = I)
X—C(17)	1.729 (6)	1.969 (8)	2.15 (1)
O—C(3)	1.385 (7)	1.372 (9)	1.37 (1)
O—C(19)	1.411 (8)	1.410 (11)	1.43 (2)
C(1)—C(2)	1.377 (7)	1.375 (10)	1.39 (1)
C(1)—C(10)	1.413 (7)	1.395 (9)	1.40 (1)
C(2)—C(3)	1.380 (8)	1.388 (11)	1.37 (2)
C(3)—C(4)	1.376 (7)	1.372 (11)	1.38 (1)
C(4)—C(5)	1.401 (7)	1.405 (10)	1.44 (1)
C(5)—C(10)	1.387 (7)	1.401 (10)	1.38 (1)
C(5)—C(6)	1.517 (7)	1.511 (10)	1.53 (1)
C(6)—C(7)	1.520 (7)	1.531 (9)	1.53 (1)
C(7)—C(8)	1.533 (6)	1.548 (9)	1.53 (1)
C(8)—C(9)	1.536 (6)	1.537 (9)	1.54 (1)
C(8)—C(14)	1.544 (6)	1.540 (9)	1.56 (1)
C(9)—C(10)	1.527 (7)	1.532 (9)	1.55 (1)
C(9)—C(11)	1.536 (7)	1.533 (11)	1.49 (1)
C(11)—C(12)	1.521 (7)	1.522 (9)	1.51 (1)
C(12)—C(13)	1.550 (7)	1.538 (9)	1.56 (1)
C(13)—C(14)	1.551 (7)	1.574 (10)	1.55 (1)
C(13)—C(17)	1.519 (8)	1.522 (10)	1.53 (1)
C(13)—C(18)	1.559 (8)	1.543 (11)	1.53 (1)
C(14)—C(15)	1.559 (6)	1.561 (9)	1.57 (1)
C(15)—C(16)	1.468 (8)	1.459 (12)	1.44 (1)
C(16)—N	1.136 (8)	1.137 (11)	1.13 (1)
C(3)—O—C(19)	118.3 (5)	118.3 (7)	118.7 (11)
C(2)—C(1)—C(10)	121.4 (5)	121.3 (7)	120.8 (11)
C(1)—C(2)—C(3)	120.0 (5)	120.6 (8)	120.9 (12)
O—C(3)—C(2)	116.0 (5)	116.2 (7)	116.6 (11)
O—C(3)—C(4)	124.0 (5)	125.0 (8)	123.5 (11)
C(2)—C(3)—C(4)	119.9 (5)	118.7 (8)	119.5 (11)
C(3)—C(4)—C(5)	120.5 (5)	121.9 (7)	119.5 (11)
C(4)—C(5)—C(6)	118.3 (5)	118.9 (7)	117.1 (9)
C(4)—C(5)—C(10)	120.5 (5)	118.9 (7)	120.4 (10)
C(6)—C(5)—C(10)	121.2 (5)	122.3 (7)	122.5 (9)
C(5)—C(6)—C(7)	113.0 (5)	112.3 (6)	111.2 (9)
C(6)—C(7)—C(8)	110.2 (4)	109.8 (6)	110.2 (8)
C(7)—C(8)—C(9)	110.0 (4)	109.6 (5)	110.6 (8)
C(7)—C(8)—C(14)	114.2 (4)	113.3 (6)	114.1 (8)
C(9)—C(8)—C(14)	108.9 (4)	109.1 (6)	108.0 (8)
C(8)—C(9)—C(10)	113.4 (4)	113.3 (6)	111.4 (8)
C(8)—C(9)—C(11)	109.7 (4)	108.8 (6)	112.2 (8)
C(10)—C(9)—C(11)	114.0 (4)	113.8 (6)	114.1 (8)
C(1)—C(10)—C(5)	117.7 (5)	118.6 (7)	118.6 (10)
C(1)—C(10)—C(9)	120.0 (5)	119.9 (6)	119.2 (9)
C(5)—C(10)—C(9)	122.1 (5)	121.4 (6)	122.2 (9)
C(9)—C(11)—C(12)	110.1 (4)	110.1 (7)	111.3 (9)
C(11)—C(12)—C(13)	114.0 (5)	113.1 (6)	113.4 (8)
C(12)—C(13)—C(14)	109.0 (4)	108.6 (6)	109.0 (8)
C(12)—C(13)—C(17)	108.3 (5)	109.4 (6)	108.6 (8)
C(12)—C(13)—C(18)	108.8 (5)	109.7 (6)	108.5 (9)
C(14)—C(13)—C(17)	113.0 (5)	112.3 (6)	112.8 (9)
C(14)—C(13)—C(18)	112.9 (5)	113.3 (6)	113.1 (9)
C(17)—C(13)—C(18)	104.7 (5)	103.5 (6)	104.7 (9)
C(8)—C(14)—C(13)	112.1 (4)	110.9 (6)	111.5 (9)
C(8)—C(14)—C(15)	112.9 (4)	113.6 (6)	113.7 (9)
C(13)—C(14)—C(15)	114.0 (4)	113.5 (6)	113.6 (9)
C(14)—C(15)—C(16)	114.5 (5)	115.5 (7)	114.9 (9)
C(15)—C(16)—N	177.4 (11)	178.8 (10)	178.5 (14)
X—C(17)—C(13)	115.6 (4)	115.3 (5)	116.9 (7)
C(2)—C(3)—O—C(19)	179.1 (6)	179.4 (8)	180.0 (12)
C(11)—C(12)—C(13)—C(18)	71.5 (6)	70.3 (8)	70.9 (11)
C(11)—C(12)—C(13)—C(17)	−175.3 (5)	−176.9 (7)	−175.9 (9)
C(12)—C(13)—C(17)—*X*	61.4 (5)	61.4 (7)	64.4 (10)
C(12)—C(13)—C(14)—C(15)	−176.6 (4)	−175.9 (6)	−174.8 (8)
C(13)—C(14)—C(15)—C(16)	−75.1 (6)	−74.8 (9)	−74.3 (12)
C(14)—C(15)—C(16)—N	126.5	138.7	147.7

The high degree of conformational similarity for all three compounds leads to only slight differences in the non-bonded O···*X* distances: 10.383 (8) Å for the chloride, 10.490 (7) Å for the bromide and 10.668 (9) Å for the iodide derivative. Fig. 2(*a*) and (*b*) represents the superimposition of chloride (solid line), bromide (dashed line) and iodide (dotted line) compounds viewed perpendicular to the C(8)—C(14) bond and along C(10)···C(13), respectively.

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* Lists of structure factors, anisotropic thermal parameters, agonistic and antagonistic activities and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54901 (32 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 3. *Ring puckering parameters* [Q(Å), φ(°), θ(°)], *lowest asymmetry parameters* [ΔC_s, ΔC_2(°)] *and lowest asymmetry factors* [fC_s, fC_2 (Å × 10^{-2})] *for B and C rings in* (1), (2) *and* (3)

		Q	φ	θ	ΔC_s	ΔC_2	fC_s	fC_2
B	(1)	0.378 (6)	324 (1)	131.1 (7)	17.3[C(7)]	5.9[C(7)—C(8)]	15.6[C(7)]	3.1[C(7)—C(8)]
	(2)	0.388 (9)	325 (1)	131.2 (9)	18.3[C(7)]	4.9[C(7)—C(8)]	16.4[C(7)]	2.7[C(7)—C(8)]
	(3)	0.39 (1)	326 (2)	130 (1)	19.7[C(7)]	4.3[C(7)—C(8)]	17.0[C(7)]	2.4[C(7)—C(8)]
C	(1)	0.063 (7)	210 (6)	173.9 (6)	4.1[C(8)]	1.4[C(8)—C(9)]	2.6[C(8)]	0.0[C(8)—C(9)]
					2.7[C(9)]	6.7[C(9)—C(11)]	2.6[C(9)]	4.4[C(9)—C(11)]
					6.8[C(11)]	7.5[C(11)—C(12)]	6.3[C(11)]	4.4[C(11)—C(12)]
	(2)	0.05 (1)	210 (13)	175 (1)	4.1[C(8)]	2.1[C(8)—C(9)]	2.2[C(8)]	0.0[C(8)—C(9)]
					1.8[C(9)]	5.4[C(9)—C(11)]	2.2[C(9)]	3.8[C(9)—C(11)]
					5.9(C(11)]	7.0[C(11)—C(12)]	5.4[C(11)]	3.8[C(11)—C(12)]
	(3)	0.05 (2)	174 (18)	175 (2)	1.8[C(8)]	0.8[C(8)—C(9)]	0.4[C(8)]	2.4[C(8)—C(9)]
					3.0[C(9)]	5.5[C(9)—C(11)]	3.7[C(9)]	4.0[C(9)—C(11)]
					4.8[C(11)]	4.6[C(11)—C(12)]	4.0[C(11)]	1.6[C(11)—C(12)]

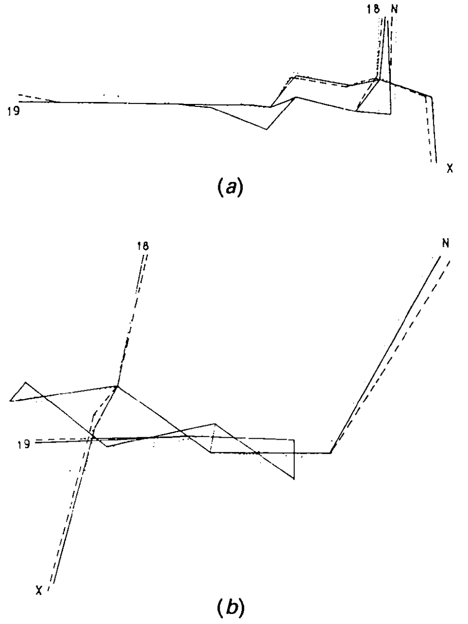

Fig. 2. Superimposed fit of chloride (solid), bromide (dashed) and iodide (dotted) molecules (*a*) viewed perpendicular to the C(8)—C(14) bond and (*b*) viewed along the C(10)···C(13) direction.

The conformations of the major parts of the molecules are similar to that of the well known steroid estrogen, estradiol (Fullerton, 1977; Duax, Weeks, Rohrer & Griffin, 1977). The estradiol molecule is able to attach, *via* hydrogen bonds, two water molecules to the O atom at C(17). This increases the initial length of 10.9 Å between the O atoms at C(3) and C(17) to 12.1 Å, *i.e.* between the O atom at C(3) and one water molecule, which is critical for receptor binding. In contrast, substitution of O in the 17-hydroxy moiety with halogen elements (Cl, Br, I) does not allow any hydrogen bonds and, subsequently, estrogen activity. Thus, although the phenolic ring *A* in this type of steroid is critical to the initiation of estrogen receptor binding (Duax, Griffin & Ebright, 1985), the newly synthesized 17-(chloro, bromo,iodo)-3-methoxy-16,17-secoestra-1,3,5(10)-triene-16-nitrile molecules show, especially for high dosages, a complete loss of estrogenic activity.

The 17-halogeno derivatives were submitted to a biological screening of their possible antiestrogenic activities (Wakeling, O'Connor & Newboult, 1983). Compounds (1) and (3) exhibit no antagonistic activities, while the bromo derivative (2) exhibits nearly 25% antagonistic action.*

Since the X···O distances, especially Cl···O and Br···O, are rather similar, the antagonistic property of (2) can presumably be attributed to the transitional electronegativity and polarizability of Br between Cl and I.

The absence of hydroxy groups at C(3) and C(17) results in no hydrogen bonding between molecules. The molecules have only normal van der Waals contacts with their surroundings.

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* Lists of agonistic and antagonistic activities for all three compounds have been deposited.

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Structure of 6-(*tert*-Butylimino)-4,4,5,5-tetracyano-3-(1-phenylethylidene)-1-(trimethylsilyl)cyclohex-1-ene

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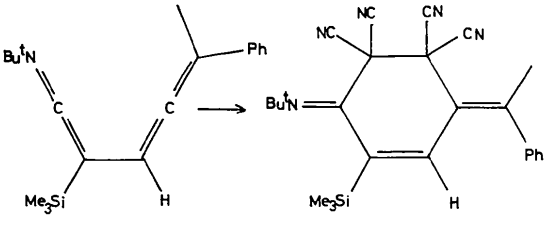
Abstract. 6-(*tert*-Butylimino)-3-(1-phenylethylidene)-1-(trimethylsilyl)-1-cyclohexene-4,4,5,5-tetracarbonitrile, $C_{25}H_{27}N_5Si$, $M_r = 425.61$, orthorhombic, *Pbca*, $a = 16.454$ (3), $b = 17.353$ (3), $c = 17.674$ (1) Å, $V = 5046.4$ Å^3, $Z = 8$, $D_m = 1.11$ (2), $D_x = 1.120$ g cm^{-3}, λ(Mo $K\alpha$) = 0.71069 Å, $\mu = 0.83$ cm^{-1}, $F(000) = 1808$, ambient temperature, $R = 0.063$ for 2891 observed [$F > 2\sigma(F)$] reflections. The heavy substitution on the cyclohexene ring distorts the imino group out of conjugation with the ring double bond.

Introduction. We have been investigating the use of titanocene vinylidene complexes generated *in situ* from the 1-dimethylalumino-1-bis(cyclopentadienyl)-chlorotitanoalkenes for the carbometallation of unactivated alkenes and alkynes (Dennehy & Whitby, 1990). The intramolecular addition of these reagents to alkynes affords titanocyclobutenes which undergo an unusual reaction with ^{t}BuNC to give unstable allenyl ketenimines (Dennehy & Whitby, 1992). Compound (I) was isolated as the stable tetracyanoethylene adduct (II) which gave crystals suitable for X-ray examination, and the structure is reported herein.



(I) (II)

Experimental. Colourless crystal (0.25 × 0.37 × 0.20 mm), from 40–60 petroleum ether–diethyl ether, mounted in glass capillary. Preliminary photographic X-ray examination. Density by flotation (CCl_4–hexane). Enraf–Nonius FAST area detector diffractometer using graphite-monochromated Mo $K\alpha$ radiation and a crystal to detector distance of 40 mm [refined to 40.38 (2) mm]. Unit-cell parameters and orientation matrix from 250 reflections. 19 281 reflections measured (one hemisphere, $2\theta_{max} = 53.5°$) and processed using the *ABSURD* software package, Lorentz and polarization corrections, no absorption or decay correction (Danopoulos, Wilkinson, Hussain-Bates & Hursthouse, 1991). Space group *Pbca* (No. 61) from systematic absences, 4559 unique reflections ($R_{int} = 0.065$), 2891 reflections with $F > 2\sigma(F)$ and $2\theta < 50°$ used (h 0–18, k 0–19, l 0–20 after transformation). Structure solution by *SHELXS86* (Sheldrick, 1986) and refined by *SHELX76* (Sheldrick, 1976) using full-matrix least squares on F. Nearly all of the H atoms appeared on a difference electron-density synthesis ($R = 0.102$) but with disorder in the trimethylsilyl and *tert*-butyl residues. Final $R = 0.063$, $wR = 0.067$, 303 parameters, anisotropic (C, N, Si) and isotropic (H) atoms, H atoms in calculated positions [C—H = 0.95 Å], $w = [\sigma^2(F) + 0.00015F^2]^{-1}$, $S = 0.69$. Maximum Δ/σ in final cycle 0.1, $\Delta\rho$ for final model < 0.40 and > -0.31 e Å^{-3}. Neutral-atom scattering factors and anomalous-dispersion corrections taken from *International Tables for X-ray Crystallography* (1974, Vol. IV) (Si only) and *SHELX76*. Fig. 1 was drawn using *ORTEP*II (Johnson, 1976) and all calculations were carried out on an IBM 3090 computer.

Discussion. Atomic coordinates for non-H atoms are listed in Table 1 and bond lengths and angles appear

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