Successive cross-linking would form polymer molecules with chain axes parallel to a. There is sufficient freedom for the diacetylene segments of 3,5-octadiyne-1,8-diol to be rearranged during polymerization without the series of hydrogen bonds (illustrated by the broken lines in Fig. 3) being disrupted. This contrasts significantly with the behaviour of 2,4-hexadiyn-1-ol (Fisher, Batchelder & Hursthouse, 1978) where rather severe hydrogen-bonding restrictions at one end of each monomer molecule affect the polymerization process. Crystallographic studies of polymeric 3,5-octadiyne-1,8-diol are in progress.

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Conformational Analysis of Progestational Agents: 11β-Fluoro-19-nor-17α-pregn-4-en-20-yn-17β-ol

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Abstract. $C_{20}H_{27}FO$, $M_r = 302.4$, monoclinic, $P2_1$, $a = 10.2844$ (7), $b = 11.2118$ (6), $c = 7.2248$ (4) Å, $\beta = 94.604$ (5)° ($\lambda = 1.5418$ Å, T = room temperature), $V = 830.4$ Å³, $Z = 2$, $\rho_x = 1.210$ g cm⁻³. The 11β-fluoro substituent places about the same steric strain on the molecule as H. The result in overall conformation is essentially the same as the unsubstituted compound without the bowing caused by other 11β substituents.

Introduction. A correlation between the steric size of the 11β substituent and the progestational activity of lynestrenol derivatives has been proposed (van der Broek *et al.*, 1977) and the variation in activity appears related to changes in the overall conformation of the molecule caused by the introduction of the 11β substituent rather than to the direct interaction of the 11β substituent with the receptor site. Because the progestational activity of the title compound is only slightly enhanced by 11β-fluoro substitution, it is of interest to compare its conformation with that of lynestrenol.

Crystal data were measured on a crystal of dimensions $0.20 \times 0.50 \times 0.80$ mm on an Enraf–Nonius CAD-4 automatic diffractometer using Ni-filtered Cu $K\alpha$ radiation. The condition $k = 2n$ limiting the $0k0$ reflections determined the space group to be $P2_1$. The lattice parameters were refined by a least-squares fit to measured 2θ values of 75 reflections in the range $49 < 2\theta < 70°$. Integrated relative intensities for 1784 independent reflections with $2\theta < 150°$ were measured using ω–2θ scans; 1746 of these intensities were determined to be observed above background ($I > 2\sigma_I$).

The intensities were reduced to structure factor amplitudes, and phase angles sufficient to locate the missing F atom were derived using the coordinates of the isomorphous structure of lynestrenol (Rohrer, Lauffenburger, Duax & Zeelen, 1976). The H atoms

were located on a difference electron density map prepared at an intermediate stage of least-squares refinement of the structural parameters. In the final cycles of full-matrix least-squares refinement, positional parameters for all atoms, anisotropic thermal parameters for the nonhydrogen atoms, and isotropic thermal parameters for the H atoms were determined. The quantities $(1/\sigma_F^2)$, where σ_F was defined by Stout & Jensen (1968, p. 457, equation H14) but with an instability factor of 0·06, were used to weight the least-squares differences for the observed data; the unob-

served data were given zero weight. The final values of the residual, $R = \sum||F_o| - |F_c||/\sum|F_o|$, were 0·041 for the observed data and 0·042 for all data measured. Final positional parameters are listed in Table 1.*

Discussion. The structure of the molecule and atomic numbering are shown in Fig. 1. The intramolecular dimensions involving the nonhydrogen atoms are given in Fig. 2. The largest estimated standard deviation for the bond lengths is 0·004 Å, for the bond angles 0·2°. The 26 C—H bond distances range from 0·81 to 1·14 Å. The O—H bond distance is 0·98 Å. All of the bond lengths and angles in this structure are very similar to those observed in other lynestrenol derivative structures. The nonbonded contact distances less than 3·5 Å all involve F(11β) with C(4), C(6) and C(21) of a symmetry $(-x, \frac{1}{2} + y, 1 - z)$ related molecule. The contact distances are 3·478, 3·462 and 3·163 Å respectively. The 17β-hydroxyl has no contact distance short enough to be considered a hydrogen bond. The 17β-hydroxyl in the crystal structure of lynestrenol also does not form a hydrogen bond.

The Δ^4 A ring has a 1α,2β-half-chair conformation as indicated by the ΔC_2(C 1–C 2) (Duax, Weeks & Rohrer, 1976) value of 4·2°. This is very similar to the A-ring conformation in lynestrenol with ΔC_2(C 1–C 2) equaling 5·8°. The nonbonded intramolecular contact distance

Table 1. *Atomic coordinates of* 11β-*fluoro*-19-*nor*-17α-*pregn*-4-*en*-20-*yn*-17β-*ol*

	x	y	z
C(1)	0·1009 (2)	0·1667 (2)	0·1283 (2)
C(2)	−0·0329 (2)	0·1255 (2)	0·0419 (3)
C(3)	−0·0423 (2)	−0·0093 (2)	0·0603 (3)
C(4)	−0·0001 (2)	−0·0500 (2)	0·2534 (2)
C(5)	0·0679 (1)	0·0174 (2)	0·3813 (2)
C(6)	0·0922 (1)	−0·0227 (2)	0·5793 (2)
C(7)	0·2338 (1)	−0·0023 (2)	0·6572 (2)
C(8)	0·2763 (1)	0·1266 (1)	0·6272 (2)
C(9)	0·2588 (1)	0·1575	0·4186 (2)
C(10)	0·1158 (1)	0·1410 (1)	0·3368 (2)
C(11)	0·3109 (2)	0·2804 (1)	0·3740 (2)
C(12)	0·4479 (2)	0·3074 (1)	0·4639 (2)
C(13)	0·4660 (1)	0·2750 (1)	0·6683 (2)
C(14)	0·4190 (1)	0·1462 (1)	0·6953 (2)
C(15)	0·4661 (2)	0·1162 (2)	0·8967 (2)
C(16)	0·5944 (2)	0·1870 (3)	0·9315 (2)
C(17)	0·6095 (2)	0·2641 (2)	0·7558 (2)
C(18)	0·3946 (2)	0·3666 (2)	0·7844 (3)
C(20)	0·6925 (2)	0·2013 (2)	0·6300 (3)
C(21)	0·7601 (2)	0·1478 (2)	0·5340 (3)
F(11β)	0·2227 (1)	0·3669 (1)	0·4324 (2)
O(17β)	0·6647 (1)	0·3793 (1)	0·8010 (2)
H(1A)	0·169 (2)	0·126 (3)	0·049 (3)
H(1B)	0·117 (2)	0·253 (3)	0·108 (3)
H(2A)	−0·049 (3)	0·157 (3)	−0·089 (4)
H(2B)	−0·092 (2)	0·172 (3)	0·122 (3)
H(3A)	0·006 (4)	−0·045 (5)	−0·054 (4)
H(3B)	−0·135 (3)	−0·029 (4)	0·040 (4)
H(4)	−0·035 (2)	−0·142 (2)	0·277 (3)
H(6A)	0·061 (2)	−0·104 (2)	0·602 (3)
H(6B)	0·030 (2)	0·031 (2)	0·664 (3)
H(7A)	0·288 (2)	−0·052 (3)	0·583 (3)
H(7B)	0·249 (2)	−0·022 (2)	0·785 (3)
H(8B)	0·226 (2)	0·181 (3)	0·692 (3)
H(9A)	0·320 (2)	0·097 (2)	0·347 (3)
H(10B)	0·067 (2)	0·197 (2)	0·405 (2)
H(11A)	0·308 (3)	0·296 (3)	0·231 (3)
H(12A)	0·512 (2)	0·270 (2)	0·393 (3)
H(12B)	0·474 (2)	0·395 (2)	0·449 (3)
H(14A)	0·477 (2)	0·098 (3)	0·603 (3)
H(15A)	0·490 (3)	0·026 (4)	0·919 (4)
H(15B)	0·390 (3)	0·139 (3)	0·997 (3)
H(16A)	0·663 (3)	0·153 (4)	0·961 (4)
H(16B)	0·596 (3)	0·236 (3)	1·058 (4)
H(18A)	0·305 (2)	0·367 (3)	0·769 (3)
H(18B)	0·401 (3)	0·359 (3)	0·921 (4)
H(18C)	0·418 (3)	0·435 (3)	0·773 (4)
H(21)	0·805 (3)	0·100 (3)	0·458 (4)
H(O17)	0·756 (3)	0·378 (4)	0·773 (4)

Fig. 1. *ORTEP* (Johnson, 1965) drawings of 11β-fluoro-lynestrenol. Thermal ellipsoids for nonhydrogen atoms are scaled to 60% probability and hydrogen atoms are represented as spheres equivalent to $B = 1$ Å².
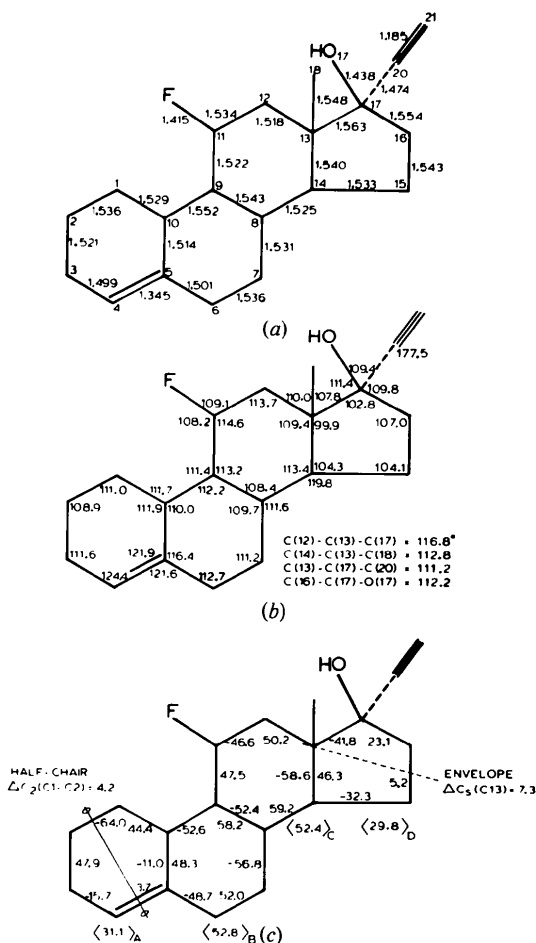
(a)

(b)

(c)

Fig. 2. Intramolecular dimensions of 11β-fluorolynestrenol. (a) Bond distances (Å); σ range = 0·002–0·004 Å. (b) Bond angles (°); σ range = 0·1–0·2°. (c) Endocyclic torsion angles (°). A torsion angle α−β−γ−δ is positive if, when viewed down the β−γ bond, the α−β bond will eclipse the γ−δ bond when rotated less than 180° in a clockwise direction. The numbers in brackets, ⟨ ⟩, are the average intra-ring dihedral angles.

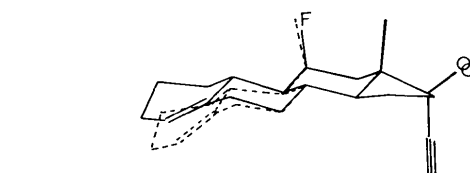

Fig. 3. Superposition of the C and D rings in the structure of the 11β-fluoro and 11β-methyl derivatives of lynestrenol.

between the axial 11β-fluoro substituent and the axial C(18) is 2·975 Å. This is only slightly longer than the 11β-hydrogen to C(18) distance of 2·84 Å in lynestrenol. This similarity in overall conformation of the 9α-fluorolynestrenol and lynestrenol is consistent with the similarity of their progestational activity when contrasted with the more active 11β-methyllynestrenol structure (Rohrer, Hazel, Duax & Zeelen, 1976) which has a bowed conformation (Fig. 3). The D ring has a C(13) β conformation.

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5,5'-Dithiobis(3-methyl-1,3,4-thiadiazoline-2-thione)

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Abstract. $C_6H_6N_4S_6$, $M_r = 326·53$, monoclinic, $C2/c$, $a = 20·08$ (2), $b = 5·150$ (5), $c = 12·17$ (1) Å, $\beta = 97·60$ (6)°, $D_x = 1·79$, $D_c = 1·74$ Mg m^{-3}, $Z = 4$. The 1,3,4-thiadiazoline ring is planar and the bond lengths show that it has extensive conjugation.

Introduction. In the study of the reaction between thiophosgene and hydrazines (Anthoni, Dahl, Eggert, Larsen & Nielsen, 1976), which mainly produces trithiocarbonates, the title compound was obtained as a byproduct. The structure analysis was undertaken to