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N^1-Acetyl-3′-methylandrosta-4,16-dieno[16,17-*d*]pyrazole-3-one

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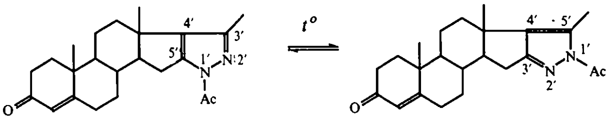
Abstract

In an attempt to find the structural features promoting the thermal isomerization of the *N*-acylated steroid[16,17-*d*]pyrazoles into [17,16-*c*]pyrazole derivatives, the X-ray structure analysis of the title compound, $C_{23}H_{30}N_2O_3$, (I), has been carried out. The steroid moiety of (I) has the usual conformation. The dihedral angle between the planar pyrazole ring and the *N*-acetyl group is very small [5.6 (2)°], but the amide C—N bond seems to be substantially elongated [1.404 (3) Å]. The *d*-pyrazole ring junction *via* a double bond leads to deformations of some bond and torsion angles, which would be decreased in the case of a ring junction *via* a single bond in the [17,16-*c*]pyrazole isomer.

Comment

The synthesis and the property studies of biologically active (Terjokhina *et al.*, 1976) *N*-acylated steroid[16,17-*d*]pyrazoles showed, unexpectedly, that their stability depends on the nature of the *N*-acyl substituent and the structure of the steroid skeleton. Thus, the *N*-acetyl derivative of androst-5-ene-3β-ol[16,17-*d*]-3′-methylpyrazole and its 3-acetate are quite stable within a wide temperature range. Their Δ^4-3-keto analogue shows notable isomerization to *N*-acetylandrost-4-ene-3-one[17,16-*c*]-5′-methylpyrazole only at 453–473 K. At the same time, the *N*-propionyl and *N*-benzoyl derivatives, and likewise *N*-acetyl-$\Delta^{4,6}$-androstapyrazoles give an equilibrium mixture of isomers at only 323–333 K.



(I)

This difference in the stability of the *N*-acyls of steroid[16,17-*d*]pyrazoles is probably a result of steric factors, in particular, repulsions between the *N*-acyl group and the steroid moiety. In an attempt to confirm this notion or to find some other features which may be responsible for stability differences, we have undertaken the structural investigation of the moderately stable title compound, (I) (Klimova, 1965; Kamernitzky, Skorova & Vesela, 1994).

The steroid moiety of (I) (Fig. 1) has the usual structure (Duax & Norton, 1975): the *A*-ring conformation is close to a 1α-sofa with some distortions towards a 1α,2β-half-chair, the *B* and *C* rings have chair conformations, and the *D* ring adopts a 14α-envelope conformation with a contribution from a 13β,14α-half-chair shape (see endocyclic torsion angles in Table 2). The π-conjugated pyrazole ring has a planar conformation (Table 2), showing substantially localized double bonds despite the ring aromaticity [C(16)=C(17) 1.353 (3) and N(20)=C(20) 1.327 (3) Å, compared to C(17)—C(20) 1.424 (3) and N(16)—C(16) 1.375 (2) Å, respectively].

The π-systems of the pyrazole ring and the *N*-acyl substituent seem to be conjugated, as manifested by a small dihedral angle [5.6 (2)°] between their mean planes. However, the amide bond length N(16)—C(22) [1.404 (3) Å] is substantially elongated compared to the

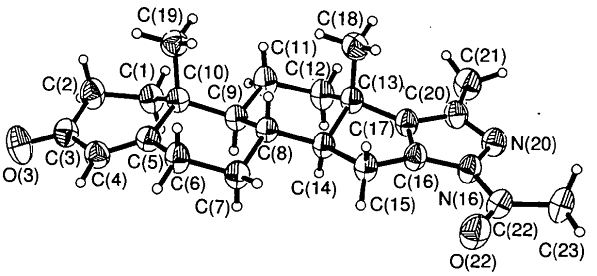


Fig. 1. Perspective view of molecule (I) showing the labelling of the non-H atoms. Displacement ellipsoids are plotted at the 50% probability level.

standard value of 1.346 Å (Allen *et al.*, 1987). This elongation is in line with the enhanced chemical mobility of *N*-acyl groups in the compounds under consideration, although it may not be attributed to steric hindrance; among observed intramolecular contacts involving this group only one, C(15)···O(22) 3.138 (3) Å, may be considered as slightly shortened in comparison with the corresponding sum of the van der Waals radii (3.22 Å; Bondi, 1964). Such repulsive contact, however, may easily explain the difference between the exocyclic bond angles at the acylated N atom [127.7 (2) and 121.8 (2)°; Table 2].

The fusion of the pyrazole ring with the *D* ring of the steroid nucleus seems to cause considerable strain. Indeed, despite the planar conformation of the pyrazole ring, a notable twist [5.0 (3)°] around the C(16)═C(17) double bond in the *D* ring persists, which reflects the tendency of this ring to form a 13*β*,14*α*-half-chair conformation, which is more sterically favourable than a 14*α*-envelope. Moreover, the fusion of two five-membered rings *via* a double bond leads to strong bond-angle deformations. For example, the exocyclic bond angles C(15)—C(16)—N(16) and C(13)—C(17)—C(20) opposite the double bond are expanded to 137.9 (2) and 142.2 (2)°, respectively, compared to a corresponding standard value of *ca* 116° in ethylenes (Gillespie & Hargittai, 1991). In this respect, the fusion of the rings in the [16,17-*c*]pyrazole isomer *via* the single bond should be more favourable, because it applies less restrictions on the flexibility of the *D* ring. However, the available structural data does not allow an explanation of the influence which the *N*-acyl substituent may have on the feasibility of the isomerization.

Experimental

The compound was prepared as described by Klimova (1965) and Kamernitzky, Skorova & Vesela (1994). It was crystallized from aqueous methanol by slow evaporation; m.p. 466–496 K.

Crystal data

$C_{23}H_{30}N_2O_3$
$M_r = 382.49$
Monoclinic
$P2_1$
$a = 10.793$ (2) Å
$b = 8.168$ (2) Å
$c = 11.289$ (2) Å
$\beta = 91.30$ (3)°
$V = 995.0$ (4) Å^3
$Z = 2$
$D_x = 1.277$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 24 reflections
$\theta = 12$–12.5°
$\mu = 0.084$ mm^{-1}
$T = 293$ (2) K
Well formed plates
0.4 × 0.4 × 0.2 mm
Colourless

Data collection

Hilger–Watts Y/290 diffractometer
$\theta/2\theta$ scans
Absorption correction: none
2691 measured reflections
2567 independent reflections
2513 observed reflections [$I > 2\sigma(I)$]

$R_{\rm int} = 0.0161$
$\theta_{\rm max} = 29.98$°
$h = 0 \rightarrow 15$
$k = 0 \rightarrow 11$
$l = -15 \rightarrow 15$
3 standard reflections monitored every 97 reflections
intensity variation: 2.3%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.051$
$wR(F^2) = 0.127$
$S = 1.053$
2564 reflections
243 parameters
$w = 1/[\sigma^2(F_o^2) + (0.1135P)^2 + 0.0031P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} = -0.096$
$\Delta\rho_{\rm max} = 0.227$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.376$ e Å^{-3}

Extinction correction: none
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)
Absolute configuration: assigned to agree with the known chirality of the steroid moiety (Duax & Norton, 1975)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
C(1)	0.3409 (2)	0.3462 (3)	0.4534 (2)	0.0463 (4)
C(2)	0.3899 (3)	0.2837 (4)	0.5722 (2)	0.0542 (5)
C(3)	0.3416 (2)	0.1169 (4)	0.6021 (2)	0.0454 (4)
C(4)	0.3033 (2)	0.0117 (3)	0.5027 (2)	0.0439 (4)
C(5)	0.3135 (2)	0.0548 (3)	0.3887 (2)	0.0385 (4)
C(6)	0.2911 (2)	−0.0702 (3)	0.2923 (2)	0.0451 (4)
C(7)	0.2135 (2)	−0.0034 (3)	0.1884 (2)	0.0439 (4)
C(8)	0.2703 (2)	0.1537 (3)	0.14120 (15)	0.0352 (3)
C(9)	0.2770 (2)	0.2832 (3)	0.2418 (2)	0.0357 (3)
C(10)	0.3566 (2)	0.2237 (3)	0.3508 (2)	0.0367 (3)
C(11)	0.3154 (2)	0.4557 (3)	0.2001 (2)	0.0487 (5)
C(12)	0.2473 (2)	0.5151 (3)	0.0868 (2)	0.0479 (5)
C(13)	0.2541 (2)	0.3857 (3)	−0.0103 (2)	0.0390 (4)
C(14)	0.1939 (2)	0.2273	0.0397 (2)	0.0370 (3)
C(15)	0.1567 (2)	0.1202 (3)	−0.0693 (2)	0.0426 (4)
C(16)	0.1278 (2)	0.2562 (3)	−0.1544 (2)	0.0420 (4)
C(17)	0.1744 (2)	0.4036 (3)	−0.1216 (2)	0.0409 (4)
C(18)	0.3884 (2)	0.3608 (4)	−0.0502 (2)	0.0511 (5)
C(19)	0.4953 (2)	0.2085 (4)	0.3210 (2)	0.0483 (5)
C(20)	0.1489 (2)	0.5122 (4)	−0.2178 (2)	0.0440 (4)
C(21)	0.1761 (3)	0.6902 (4)	−0.2271 (3)	0.0606 (6)
C(22)	0.0168 (2)	0.1542 (4)	−0.3361 (2)	0.0460 (4)
C(23)	−0.0197 (3)	0.2046 (4)	−0.4590 (2)	0.0589 (6)
O(3)	0.3404 (2)	0.0671 (3)	0.70386 (13)	0.0662 (5)
O(22)	0.0005 (2)	0.0199 (3)	−0.2957 (2)	0.0658 (5)
N(16)	0.0757 (2)	0.2743 (3)	−0.26591 (14)	0.0433 (4)
N(20)	0.0881 (2)	0.4345 (3)	−0.3046 (2)	0.0459 (4)

Table 2. *Bond lengths* (Å), *bond angles* (°) *and selected torsion angles* (°)

C(1)—C(2)	1.519 (3)	C(12)—C(13)	1.525 (3)
C(1)—C(10)	1.543 (3)	C(13)—C(17)	1.514 (2)
C(2)—C(3)	1.501 (4)	C(13)—C(18)	1.541 (3)
C(3)—O(3)	1.219 (3)	C(13)—C(14)	1.560 (3)
C(3)—C(4)	1.465 (3)	C(14)—C(15)	1.556 (2)
C(4)—C(5)	1.341 (3)	C(15)—C(16)	1.496 (3)
C(5)—C(6)	1.508 (3)	C(16)—C(17)	1.353 (3)
C(5)—C(10)	1.521 (3)	C(16)—N(16)	1.375 (2)
C(6)—C(7)	1.526 (3)	C(17)—C(20)	1.424 (3)
C(7)—C(8)	1.524 (3)	C(20)—N(20)	1.327 (3)
C(8)—C(14)	1.520 (2)	C(20)—C(21)	1.488 (3)
C(8)—C(9)	1.552 (2)	C(22)—O(22)	1.202 (3)

C(9)—C(11)	1.545 (3)	C(22)—N(16)	1.404 (3)
C(9)—C(10)	1.562 (2)	C(22)—C(23)	1.491 (3)
C(10)—C(19)	1.547 (3)	N(16)—N(20)	1.387 (3)
C(11)—C(12)	1.540 (3)		
C(2)—C(1)—C(10)	113.7 (2)	C(17)—C(13)—C(18)	106.9 (2)
C(3)—C(2)—C(1)	112.8 (2)	C(12)—C(13)—C(18)	111.3 (2)
O(3)—C(3)—C(4)	121.2 (2)	C(17)—C(13)—C(14)	98.43 (14)
O(3)—C(3)—C(2)	121.7 (2)	C(12)—C(13)—C(14)	106.72 (15)
C(4)—C(3)—C(2)	117.0 (2)	C(18)—C(13)—C(14)	113.5 (2)
C(5)—C(4)—C(3)	123.6 (2)	C(8)—C(14)—C(15)	120.01 (15)
C(4)—C(5)—C(6)	120.0 (2)	C(8)—C(14)—C(13)	112.15 (14)
C(4)—C(5)—C(10)	122.7 (2)	C(15)—C(14)—C(13)	106.42 (14)
C(6)—C(5)—C(10)	117.1 (2)	C(16)—C(15)—C(14)	97.84 (15)
C(5)—C(6)—C(7)	112.9 (2)	C(17)—C(16)—N(16)	107.2 (2)
C(6)—C(7)—C(8)	110.6 (2)	C(17)—C(16)—C(15)	114.5 (2)
C(14)—C(8)—C(7)	112.35 (14)	N(16)—C(16)—C(15)	137.9 (2)
C(14)—C(8)—C(9)	107.31 (14)	C(16)—C(17)—C(20)	106.3 (2)
C(7)—C(8)—C(9)	109.28 (14)	C(16)—C(17)—C(13)	110.0 (2)
C(11)—C(9)—C(8)	113.99 (14)	C(20)—C(17)—C(13)	142.2 (2)
C(11)—C(9)—C(10)	112.1 (2)	N(20)—C(20)—C(17)	110.4 (2)
C(8)—C(9)—C(10)	112.34 (15)	N(20)—C(20)—C(21)	120.7 (2)
C(5)—C(10)—C(1)	109.7 (2)	C(17)—C(20)—C(21)	128.8 (2)
C(5)—C(10)—C(19)	107.0 (2)	O(22)—C(22)—N(16)	119.4 (2)
C(1)—C(10)—C(19)	109.8 (2)	O(22)—C(22)—C(23)	124.6 (2)
C(5)—C(10)—C(9)	109.69 (15)	N(16)—C(22)—C(23)	116.0 (2)
C(1)—C(10)—C(9)	108.8 (2)	C(16)—N(16)—N(20)	110.4 (2)
C(19)—C(10)—C(9)	111.8 (2)	C(16)—N(16)—C(22)	127.7 (2)
C(12)—C(11)—C(9)	114.5 (2)	N(20)—N(16)—C(22)	121.8 (2)
C(13)—C(12)—C(11)	110.4 (2)	C(20)—N(20)—N(16)	105.6 (2)
C(17)—C(13)—C(12)	119.6 (2)		

C(10)—C(1)—C(2)—C(3)	−50.9 (3)
C(1)—C(2)—C(3)—C(4)	25.5 (3)
C(2)—C(3)—C(4)—C(5)	2.4 (3)
C(3)—C(4)—C(5)—C(10)	−5.0 (3)
C(4)—C(5)—C(10)—C(1)	−19.8 (3)
C(5)—C(10)—C(1)—C(2)	47.1 (3)
C(10)—C(5)—C(6)—C(7)	−47.7 (3)
C(5)—C(6)—C(7)—C(8)	53.5 (2)
C(6)—C(7)—C(8)—C(9)	−59.4 (2)
C(7)—C(8)—C(9)—C(10)	59.5 (2)
C(8)—C(9)—C(10)—C(5)	−50.9 (2)
C(9)—C(10)—C(5)—C(6)	45.4 (2)
C(14)—C(8)—C(9)—C(11)	−49.6 (2)
C(8)—C(9)—C(11)—C(12)	46.3 (2)
C(9)—C(11)—C(12)—C(13)	−50.8 (3)
C(11)—C(12)—C(13)—C(14)	58.6 (2)
C(12)—C(13)—C(14)—C(8)	−67.3 (2)
C(13)—C(14)—C(8)—C(9)	61.2 (2)
C(17)—C(13)—C(14)—C(15)	35.2 (2)
C(13)—C(14)—C(15)—C(16)	−32.2 (2)
C(14)—C(15)—C(16)—C(17)	17.2 (2)
C(15)—C(16)—C(17)—C(13)	5.0 (3)
C(16)—C(17)—C(13)—C(14)	−24.7 (2)
N(16)—C(16)—C(17)—C(20)	−0.2 (2)
C(16)—C(17)—C(20)—N(20)	0.7 (2)
C(17)—C(20)—N(20)—N(16)	−0.9 (2)
C(20)—N(20)—N(16)—C(16)	0.8 (2)
N(20)—N(16)—C(16)—C(17)	−0.4 (2)
C(16)—N(16)—C(22)—O(22)	5.2 (4)
N(20)—N(16)—C(22)—C(23)	6.0 (3)

Program(s) used to solve structure: *SHELXTL-Plus* (Sheldrick, 1987). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993).

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Lists of structure factors, anisotropic displacement parameters and H-atom coordinates have been deposited with the IUCr (Reference: AB1175). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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1,6-Dimethyltetrahydroimidazo[4,5-*d*]-imidazole-2,5(1*H*,6*H*)-dione Monohydrate

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Abstract

The bicyclic system of the title compound, $C_6H_{10}N_4O_2 \cdot H_2O$, (I), consists of two planar five-membered heterocycles (maximum deviations of atoms from the mean planes do not exceed 0.03 Å). The dihedral angle formed by the average mean planes of the rings is 121.4 (1)°. Bond lengths and angles in (I) are in good agreement with the relevant parameters of acyclic urea derivatives.

Comment

The title compound (I), prepared according to Nematollahi & Ketcham (1963), belongs to the class of bicyclic bisurea (BBU) derivatives of the general formula (II), where R^1, R^2, R^3 and R^4 = H, alkyl, and R^5 and R^6 = H, CH_3, which exhibit strong psychotropic activity. It has been shown that the type and degree of pharmacological activity depends on the nature and the number of substituents in the BBU molecule (Suvorova, Yeres'ko, Yepishina, Lebedev & Khmelnitsky, 1979). Among the

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