$a = 14.502$ (2) Å
$b = 10.904$ (3) Å
$c = 14.503$ (2) Å
$\beta = 90.34$ (1)°
$V = 2293.4$ (7) Å^3
$Z = 4$
$D_x = 1.351$ Mg m^{-3}

$\theta = 13.2$–$17.4°$
$\mu = 0.251$ mm^{-1}
$T = 296$ K
Cubic
0.35 × 0.35 × 0.25 mm
White

Data collection

Rigaku AFC-5*S* diffractometer
ω–2θ scans
Absorption correction: empirical, ψ-scan
$T_{\min} = 0.96$, $T_{\max} = 1.00$
2238 measured reflections
2144 independent reflections
1259 observed reflections [$I > 2\sigma(I)$]

$R_{\rm int} = 0.016$
$\theta_{\max} = 25°$
$h = -17 \rightarrow 0$
$k = -13 \rightarrow 0$
$l = -17 \rightarrow 17$
3 standard reflections monitored every 150 reflections intensity variation: ±0.5%

Refinement

Refinement on *F*
$R = 0.052$
$wR = 0.056$
$S = 1.78$
1259 reflections
175 parameters
$w = 1/\sigma^2(F)$

$(\Delta/\sigma)_{\max} = 0.01$
$\Delta\rho_{\max} = 0.27$ e Å^{-3}
$\Delta\rho_{\min} = -0.23$ e Å^{-3}
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

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

$B_{\rm eq} = (4/3)\Sigma_i\Sigma_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$

	x	*y*	*z*	$B_{\rm eq}$
S(1)	0.66990 (7)	0.3953 (1)	0.68843 (6)	5.41 (5)
O(1)	0.6261 (2)	0.7092 (3)	0.5028 (2)	6.2 (2)
O(2)	0.6503 (2)	0.6365 (3)	0.6430 (2)	7.2 (2)
C(1)	1/2	0.2337 (5)	3/4	4.1 (3)
C(2)	0.5816 (2)	0.1711 (4)	0.7348 (2)	4.3 (2)
C(3)	0.5814 (3)	0.0439 (4)	0.7347 (3)	5.3 (2)
C(4)	1/2	−0.0181 (6)	3/4	6.1 (4)
C(5)	0.6728 (3)	0.2365 (4)	0.7247 (3)	5.4 (2)
C(6)	0.6414 (2)	0.3873 (4)	0.5693 (2)	4.2 (2)
C(7)	0.6333 (3)	0.2755 (4)	0.5242 (3)	4.9 (2)
C(8)	0.6139 (3)	0.2714 (4)	0.4308 (3)	5.5 (2)
C(9)	0.6016 (3)	0.3768 (4)	0.3803 (3)	5.1 (2)
C(10)	0.6088 (3)	0.4875 (4)	0.4231 (3)	4.8 (2)
C(11)	0.6291 (2)	0.4957 (4)	0.5179 (2)	4.2 (2)
C(12)	0.6364 (2)	0.6175 (4)	0.5627 (3)	5.0 (2)
C(13)	0.6316 (4)	0.8302 (5)	0.5456 (4)	7.1 (3)
C(14)	0.6155 (4)	0.9157 (5)	0.4754 (4)	9.4 (4)

Table 2. *Selected geometric parameters* (Å, °)

S(1)—C(5)	1.810 (5)	C(6)—C(7)	1.388 (5)
S(1)—C(6)	1.776 (3)	C(6)—C(11)	1.408 (5)
O(1)—C(12)	1.332 (5)	C(7)—C(8)	1.384 (5)
O(1)—C(13)	1.461 (5)	C(8)—C(9)	1.374 (6)
O(2)—C(12)	1.198 (4)	C(9)—C(10)	1.362 (5)
C(1)—C(2)	1.386 (4)	C(10)—C(11)	1.407 (5)
C(2)—C(3)	1.386 (5)	C(11)—C(12)	1.483 (5)
C(2)—C(5)	1.510 (5)	C(13)—C(14)	1.399 (7)
C(5)—S(1)—C(6)	103.9 (2)	C(6)—C(7)—C(8)	120.4 (4)
C(12)—O(1)—C(13)	113.3 (3)	C(7)—C(8)—C(9)	121.4 (4)
C(2)—C(1)—C(2$^{\rm i}$)	120.9 (5)	C(8)—C(9)—C(10)	119.3 (4)
C(1)—C(2)—C(3)	119.4 (4)	C(9)—C(10)—C(11)	121.1 (4)
C(1)—C(2)—C(5)	122.1 (4)	C(6)—C(11)—C(10)	119.3 (3)
C(3)—C(2)—C(5)	118.3 (4)	C(6)—C(11)—C(12)	120.8 (3)
C(2)—C(3)—C(4)	119.5 (5)	C(10)—C(11)—C(12)	119.9 (4)
C(3)—C(4)—C(3$^{\rm i}$)	121.3 (6)	O(1)—C(12)—O(2)	121.5 (4)
S(1)—C(5)—C(2)	117.5 (3)	O(1)—C(12)—C(11)	112.3 (4)
S(1)—C(6)—C(7)	121.3 (3)	O(2)—C(12)—C(11)	126.3 (4)
S(1)—C(6)—C(11)	120.1 (3)	O(1)—C(13)—C(14)	106.5 (4)
C(7)—C(6)—C(11)	118.5 (3)		

Symmetry code: (i) $1 - x, y, \frac{3}{2} - z$.

The structure was solved by direct methods (Gilmore, 1984) and successive Fourier syntheses. Refinement was performed by full-matrix least-squares methods. Non-H atoms were refined with anisotropic displacement parameters and H atoms, except those of the methyl group, with fixed isotropic displacement parameters (1.2 × $B_{\rm eq}$ of the carrying atom). H atoms of the methyl group were included in the calculations in fixed positions (C—H 0.948 Å). The calculations were carried out using *TEXSAN* (Molecular Structure Corporation, 1989) on a VAXstation 3520 computer. The figure was drawn with *ORTEP*II (Johnson, 1976).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, complete geometry, including H-atom geometry, and torsion angles have been deposited with the IUCr (Reference: AB1169). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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2,6-Bis(phenylamino)pyridine

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Abstract

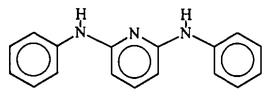
The structure of the title compound, $C_{17}H_{15}N_3$, consists of two independent molecules which are

connected by nearly linear weak N(amino)—H···N(pyridine) hydrogen bonds through a pseudo center of inversion to form a dimer. Conformationally, this symmetrically substituted pyridine derivative displays an *E*,*E* form. In this form the H-atom interactions between neighboring rings are reduced.

Comment

Aminopyridines have been studied mainly because they form part of some biologically important molecules (Schwalbe, Williams & Koetzle, 1987) and because of their ability to form metal complexes (Navarro-Ranninger, Martínez-Carrera & García-Blanco, 1985; Ray & Hathaway, 1980). We have synthesized a series of new multidentate N-donor ligands, derived from aminopyridine, in order to study their complexation behaviour.

2-Anilinopyridines show conformational isomerism (Takasuka, Nakai & Shiro, 1986). In appropriate solvents, the *E* and *Z* forms are in equilibrium. The predominant form in solution is also the predominant form found in the solid state and depends on the aniline substituents. Crystals of 2,6-bis(phenylamino)pyridine, (I), which is a symmetrically substituted 2,6-dianilinopyridine, display the *E*,*E* form. To relieve the H-atom interactions in the *E*,*E* form, *i.e.* within the atom pairs H(3)···H(20), H(5)···H(13), H(23)···H(40) and H(25)···H(29), the phenyl rings are rotated around the N(amino)—C(phenyl) bond. If the title molecule is viewed along the crystallographic *a* axis, the six-membered rings in the molecule with atom numbers 1–20 are rotated to form a left-handed screw whereas the other molecule (atoms 21–40) seen in the same direction is right handed. The dihedral angles between phenyl rings C(8)–C(13) and C(15)–C(20) and the pyridine ring are 53.4 (2) and 37.7 (2)°, respectively. In the other molecule, the corresponding angles between the C(28)–C(33) and C(35)–C(40) rings and the pyridine ring are 25.8 (2) and 51.5 (2)°, respectively. The two independent molecules form a dimer through weak hydrogen bonds, where one amino N atom is a proton donor and the pyridine N atom is an acceptor (see Table 3). The dimers are held together by weak van der Waals forces. Similar hydrogen-bonding geometries are found in several variously substituted 2-aminopyridines (Nahringbauer & Kvick, 1977) and 2,2′-dipyridylamine (Pyrka & Pinkerton, 1992). 2,6-Diaminopyridine has a slightly different hydrogen-bond pattern (Schwalbe, Williams & Koetzle, 1987).



(I)

As Schwalbe, Williams & Koetzle (1987) noticed, a single amino group attached to the pyridine ring in the 2-position is expected to show sp^2 hybridization and to make a significant contribution of *p* electrons to the π system, which increases the bond order and shortens the bond to the ring. When there are two groups in the 2- and 6-positions, the effect on each group is smaller, resulting in a slightly longer bond. The N(amino)—C(py) bonds, 1.379 (11)–1.391 (11) Å, as well as the N(amino)—C(phenyl) bonds, 1.400 (10)–1.415 (10) Å, indicate resonance interactions with the neighboring aromatic rings and a partial double-bond character of these bonds. The N—C single-bond length is 1.45 (2) Å in —C(sp^2)—N(H)—C(sp^2)— systems (*cf. International Tables for Crystallography*, 1992, Vol. C, p. 743). The sum of the bond angles around the amino N atoms N(7), N(14), N(27) and N(34) is 360 (3)°, which confirms the planar sp^2 hybridization mode to the amino N atoms.

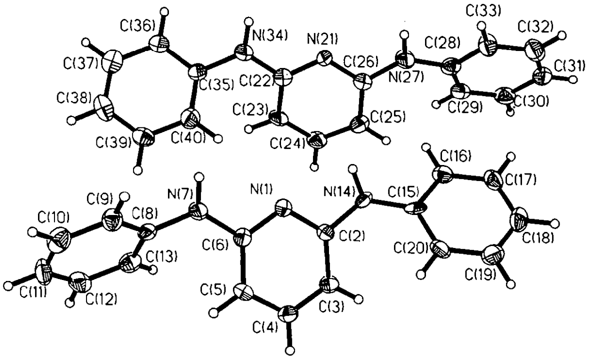


Fig. 1. The asymmetric unit composed of two molecules (*SHELXTL/PC*; Sheldrick, 1990). Displacement ellipsoids are drawn at the 30% probability level.

Experimental

The title compound was prepared by melting 2,6-dibromopyridine and aniline hydrochloride in a method analogous to that described by Hamana & Yamazaki (1961). 2,6-Dibromopyridine (3.75 g, 15.8 mmol) and aniline hydrochloride (3.51 g, 31.8 mmol) were heated in a round-bottomed flask equipped with a magnetic stirrer in an oil bath at 473 K. During heating the melt slowly turned orange. After 3 h reaction time, 75 ml water was added and the mixture was alkalized with sodium carbonate to liberate the product from its hydrohalic salt. The raw product was extracted into chloroform. After evaporation of the solvent, a yellow compound was obtained and recrystallized from a water–ethanol mixture [m.p. 375 (1) K].

Crystal data

$C_{17}H_{15}N_3$
$M_r = 261.3$
Monoclinic
$P2_1/n$

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections

$a = 16.283$ (3) Å
$b = 8.150$ (2) Å
$c = 20.697$ (4) Å
$\beta = 97.56$ (3)°
$V = 2723$ (1) Å^3
$Z = 8$
$D_x = 1.275$ Mg m^{-3}

$\theta = 5$–15°
$\mu = 0.077$ mm^{-1}
$T = 296$ K
Plate
0.50 × 0.30 × 0.15 mm
Yellow

Data collection

Rigaku AFC-7*S* diffractometer
$2\theta/\omega$ scans
Absorption correction: none
2809 measured reflections
2624 independent reflections
1277 observed reflections $[F > 4\sigma(F)]$

$R_{\rm int} = 0.014$
$\theta_{\rm max} = 26.5°$
$h = 0 \rightarrow 15$
$k = 0 \rightarrow 9$
$l = -24 \rightarrow 24$
3 standard reflections monitored every 200 reflections intensity variation: <2%

Refinement

Refinement on F
$R = 0.0542$
$wR = 0.0449$
$S = 2.16$
1277 reflections
325 parameters
$w = 1/\sigma^2(F)$

$(\Delta/\sigma)_{\rm max} = 0.354$
$\Delta\rho_{\rm max} = 0.17$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.25$ e Å^{-3}
Atomic scattering factors from *SHELXTL/PC* (Sheldrick, 1990)

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

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

	x	y	z	$U_{\rm eq}$
N(1)	0.9985 (4)	0.2804 (8)	0.3440 (3)	0.040 (3)
C(2)	1.0613 (5)	0.2916 (10)	0.3076 (4)	0.040 (4)
C(3)	1.0550 (5)	0.2481 (11)	0.2421 (3)	0.049 (4)
C(4)	0.9815 (5)	0.1796 (11)	0.2142 (4)	0.049 (4)
C(5)	0.9161 (5)	0.1629 (10)	0.2487 (4)	0.046 (4)
C(6)	0.9272 (5)	0.2198 (10)	0.3137 (4)	0.041 (4)
N(7)	0.8647 (4)	0.2088 (9)	0.3525 (3)	0.049 (3)
C(9)	0.7376 (4)	0.0680 (7)	0.3638 (2)	0.049 (4)
C(10)	0.6540	0.0357	0.3433	0.064 (5)
C(11)	0.6130	0.1163	0.2889	0.065 (5)
C(12)	0.6555	0.2290	0.2550	0.061 (4)
C(13)	0.7390	0.2613	0.2754	0.050 (4)
C(8)	0.7801	0.1808	0.3298	0.043 (4)
N(14)	1.1327 (4)	0.3582 (9)	0.3420 (3)	0.051 (3)
C(16)	1.2726 (4)	0.4507 (6)	0.3632 (2)	0.047 (4)
C(17)	1.3564	0.4372	0.3561	0.051 (4)
C(18)	1.3830	0.3124	0.3176	0.058 (4)
C(19)	1.3260	0.2013	0.2863	0.059 (4)
C(20)	1.2422	0.2149	0.2934	0.049 (4)
C(15)	1.2156	0.3396	0.3319	0.044 (4)
N(21)	1.1057 (4)	0.7639 (8)	0.4922 (3)	0.043 (3)
C(22)	1.0286 (6)	0.7866 (11)	0.4630 (4)	0.052 (4)
C(23)	1.0100 (5)	0.8394 (10)	0.3978 (4)	0.052 (4)
C(24)	1.0731 (6)	0.8564 (11)	0.3620 (4)	0.054 (4)
C(25)	1.1534 (6)	0.8262 (10)	0.3887 (4)	0.049 (4)
C(26)	1.1681 (5)	0.7850 (10)	0.4555 (4)	0.044 (4)
N(27)	1.2454 (5)	0.7549 (10)	0.4903 (3)	0.056 (3)
C(29)	1.3452 (4)	0.8935 (7)	0.4275 (3)	0.051 (4)
C(30)	1.4274	0.9154	0.4171	0.063 (4)
C(31)	1.4905	0.8303	0.4553	0.065 (4)
C(32)	1.4713	0.7235	0.5038	0.067 (5)
C(33)	1.3891	0.7016	0.5141	0.059 (4)
C(28)	1.3260	0.7866	0.4760	0.047 (4)
N(34)	0.9681 (4)	0.7545 (10)	0.5024 (3)	0.060 (3)
C(36)	0.8237 (5)	0.7902 (6)	0.5122 (2)	0.050 (4)
C(37)	0.7402	0.7592	0.4910	0.058 (4)
C(38)	0.7177	0.6608	0.4364	0.063 (4)
C(39)	0.7786	0.5934	0.4029	0.055 (4)
C(40)	0.8621	0.6244	0.4241	0.054 (4)
C(35)	0.8846	0.7228	0.4787	0.045 (4)

Table 2. *Selected geometric parameters* (Å, °)

N(1)—C(2)	1.352 (11)	N(21)—C(22)	1.333 (11)
N(1)—C(6)	1.339 (10)	N(21)—C(26)	1.357 (11)
C(2)—C(3)	1.393 (11)	C(22)—C(23)	1.411 (11)
C(2)—N(14)	1.391 (11)	C(22)—N(34)	1.385 (12)
C(3)—C(4)	1.376 (12)	C(23)—C(24)	1.350 (13)
C(4)—C(5)	1.365 (12)	C(24)—C(25)	1.373 (12)
C(5)—C(6)	1.413 (11)	C(25)—C(26)	1.412 (11)
C(6)—N(7)	1.379 (11)	C(26)—N(27)	1.388 (11)
N(7)—C(8)	1.415 (10)	N(27)—C(28)	1.407 (10)
N(14)—C(15)	1.400 (10)	N(34)—C(35)	1.406 (10)
C(2)—N(1)—C(6)	115.9 (6)	C(22)—N(21)—C(26)	117.2 (7)
N(1)—C(2)—C(3)	124.1 (7)	N(21)—C(22)—C(23)	123.2 (8)
N(1)—C(2)—N(14)	112.6 (7)	N(21)—C(22)—N(34)	114.0 (7)
C(3)—C(2)—N(14)	123.2 (8)	C(23)—C(22)—N(34)	122.8 (8)
C(2)—C(3)—C(4)	117.5 (8)	C(22)—C(23)—C(24)	118.2 (8)
C(3)—C(4)—C(5)	121.1 (7)	C(23)—C(24)—C(25)	120.9 (7)
C(4)—C(5)—C(6)	117.1 (7)	C(24)—C(25)—C(26)	117.8 (8)
N(1)—C(6)—C(5)	124.1 (8)	N(21)—C(26)—C(25)	122.4 (8)
N(1)—C(6)—N(7)	114.3 (7)	N(21)—C(26)—N(27)	112.4 (7)
C(5)—C(6)—N(7)	121.4 (7)	C(25)—C(26)—N(27)	125.1 (8)
C(6)—N(7)—C(8)	125.3 (6)	C(26)—N(27)—C(28)	131.7 (7)
N(7)—C(8)—C(9)	117.7 (3)	N(27)—C(28)—C(29)	124.7 (4)
N(7)—C(8)—C(13)	122.3 (3)	N(27)—C(28)—C(33)	115.3 (4)
C(2)—N(14)—C(15)	129.6 (6)	C(22)—N(34)—C(35)	124.0 (6)
N(14)—C(15)—C(16)	117.1 (3)	N(34)—C(35)—C(36)	118.2 (4)
N(14)—C(15)—C(20)	122.9 (3)	N(34)—C(35)—C(40)	121.8 (4)

Table 3. *Hydrogen-bonding geometry* (Å, °)

D—H···A	D—H	D···A	D—H···A
N(7)—H(7)···N(21$^{\rm i}$)	0.90 (2)	3.19 (1)	174 (2)
N(34)—H(34)···N(1$^{\rm i}$)	0.90 (2)	3.17 (1)	170 (2)

Symmetry code: (i) $2 - x, 1 - y, 1 - z$.

Data collection and cell refinement: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1993). Atomic scattering factors, structure solution, refinement, other calculations and graphics: *SHELXTL/PC* (Sheldrick, 1990). For both molecules, phenyl groups were treated as rigid groups (C—C 1.395, C—H 0.96 Å). All non-H atoms were refined anisotropically. N—H bonds were fixed to 0.90 Å, but allowed to refine. H atoms were given a common isotropic displacement factor $U_{\rm iso} = 0.08$ Å^2. Tests for observed reflections with thresholds lower than $4\sigma(F)$ gave practically no changes in the structure parameters and their e.s.d.'s despite the improved reflection-to-parameter ratio.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry, including bond distances and angles involving H atoms, have been deposited with the IUCr (Reference: AB1155). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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

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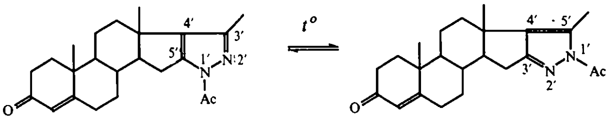
Abstract

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

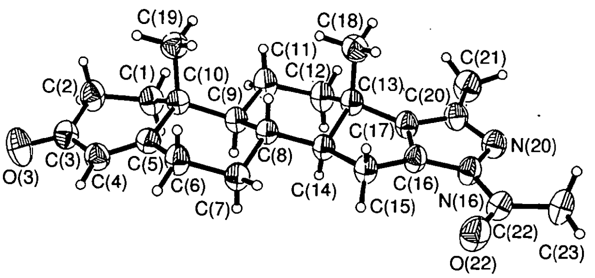


Fig. 1. Perspective view of molecule (I) showing the labelling of the non-H atoms. Displacement ellipsoids are plotted at the 50% probability level.

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