

Fig. 2. Crystallographic numbering scheme.

mination was undertaken to determine the effect of the 1 α -methyl group in a ring and the configuration at the junction of the C, D rings. The conformations of the steroid A, B and C rings are close to an ideal chair and that of the D ring is intermediate between a 13 β envelope and 13 β ,14 α half-chair. The major difference between the two independent molecules (which have the same absolute configuration) is in the direction of the hydroxyl groups. The two independent molecules are linked by one hydrogen bond of the two hydroxyl groups O(2)—H(1)···O(22) with a distance of 2.801 (3) Å. The hydroxyl H(21) atom is not involved in a hydrogen bond. The main conformational difference between the two molecules is a difference of about 6° at the B—C junction [for molecule (I) C(7)—

C(8)—C(9)—C(10) = 56.9 (3)° and C(14)—C(8)—C(9)—C(11) = -50.2 (3)°; these angles for molecule (II) are 51.4 (3) and -56.5 (3)°, respectively].

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Structure of an Indoloquinolizine Derivative

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Abstract. Racemic (2*R*,3*S*,12*bS*)-2-(1,3-dimethyl-2,4,6-trioxo-1,3-diazacyclohexyl)-3-ethyl-1,2,3,4,5,6-hexahydro-12*bH*-indolo[2,3-*a*]quinolizine methanol solvate, C₂₃H₂₈N₄O₃·CH₃OH, *M_r* = 440.5, monoclinic, *P*2₁/*n*, *a* = 11.726 (2), *b* = 15.337 (2), *c* = 12.400 (2) Å, β = 98.23 (1)°, *V* = 2207 Å³, *Z* = 4, *D_x* = 1.317 Mg m⁻³, λ (Mo *K* α) = 0.71069 Å, μ = 0.09 mm⁻¹, *F*(000) = 932, *T* = 298 K, *R* = 0.088 for 1917 observed reflections. The structure was investigated to determine the relative configuration, which could not be established unambiguously by NMR. Two different types of intermolecular hydrogen bond link the zwitterionic centres [N(4)···O(17') 2.70 (1) and

N(1)···O(24') 2.85 (1) Å]. The hydrogens bonded to nitrogen and to the oxygen of the solvent molecule were located in a difference Fourier map and refined with a common temperature factor. The solvent methanol is hydrogen bonded to a carbonyl group [O(12')···O(1x) 2.75 (1) Å].

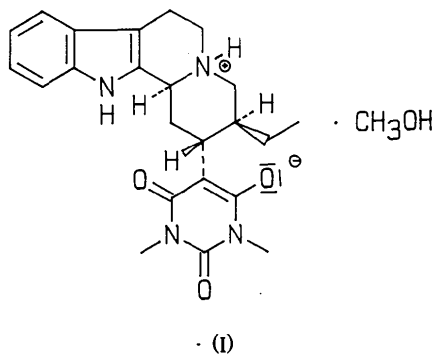
Experimental. (I): crystal size 0.2 × 0.2 × 0.6 mm. Stoe–Siemens four-circle diffractometer, monochromated Mo *K* α radiation, profile-fitting mode involving variable scan width and speed (Clegg, 1981). 4396 reflections measured, $2\theta_{\max}$ = 45°, $-12 \leq h \leq 12$, $-16 \leq k \leq 16$, $0 \leq l \leq 13$, three check reflections with

Table 1. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$)

	x	y	z	U_{eq}^*
N(1)	2260 (4)	-225 (3)	1431 (4)	43 (2)
C(2)	1158 (5)	-437 (4)	1597 (5)	34 (2)
C(3)	614 (4)	-97 (4)	2534 (4)	37 (2)
N(4)	-354 (3)	-709 (3)	2681 (4)	37 (2)
C(5)	-1145 (4)	-841 (4)	1620 (4)	43 (2)
C(6)	-557 (4)	-1284 (4)	743 (5)	44 (2)
C(7)	641 (4)	-950 (4)	774 (5)	35 (2)
C(8)	1462 (5)	-1092 (4)	39 (5)	38 (2)
C(9)	1463 (5)	-1554 (4)	-927 (5)	52 (3)
C(10)	2439 (6)	-1543 (5)	-1429 (6)	64 (3)
C(11)	3423 (6)	-1085 (5)	-982 (7)	67 (3)
C(12)	3456 (5)	-626 (5)	-17 (6)	60 (3)
O(12')	4076 (3)	-1736 (3)	4223 (4)	53 (2)
C(13)	2462 (5)	-628 (4)	481 (5)	44 (2)
C(14)	1434 (5)	-2 (4)	3595 (5)	38 (2)
C(15)	1885 (4)	-875 (4)	4061 (5)	36 (2)
C(16)	2868 (4)	-755 (4)	5000 (4)	32 (2)
C(17)	2791 (5)	-174 (4)	5838 (5)	38 (2)
O(17')	1892 (3)	239 (3)	6005 (3)	48 (2)
C(19)	1081 (7)	-2299 (6)	4888 (7)	90 (4)
C(18x)	1589 (10)	-2993 (9)	4359 (10)	90 (4)
C(18y)	1521 (23)	-2344 (18)	5836 (25)	91 (8)
C(20)	828 (5)	-1402 (4)	4302 (5)	43 (2)
C(21)	49 (5)	-1542 (4)	3232 (5)	43 (2)
C(22)	3902 (5)	-1200 (4)	4934 (5)	35 (2)
N(23)	4834 (3)	-1046 (3)	5767 (4)	38 (2)
C(23')	5914 (4)	-1517 (4)	5756 (5)	51 (3)
C(24)	4811 (5)	-439 (4)	6568 (5)	43 (3)
O(24')	5651 (3)	-302 (3)	7263 (3)	56 (2)
C(25')	3838 (5)	758 (4)	7305 (5)	56 (3)
N(25)	3811 (4)	21 (3)	6559 (4)	39 (2)
C(2x)	3623 (8)	-2547 (6)	1715 (7)	97 (4)
O(1x)	3590 (6)	-3003 (4)	2660 (5)	120 (3)

* Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

no significant intensity change. 2887 unique reflections ($R_{int} = 0.037$), of which 1917 with $F > 3\sigma(F)$ were used for all calculations (*SHELXS86*, Sheldrick, 1985; *SHELX76*, Sheldrick, 1976). Cell constants refined from $\pm 2\theta$ values of 38 reflections in the range 20 – 25° . Absorption and extinction corrections were not necessary. Structure solution by direct methods. Refinement on F to $R = 0.088$, $wR = 0.075$; all non-H atoms anisotropic; H atoms were included using a riding model [$C-H$ 0.96 \AA , $U(H) = 0.08 \text{ \AA}^2$], except for methyl protons $U(H) = 0.12 \text{ \AA}^2$, 288 parameters, $S = 1.67$, weighting scheme $w^{-1} = \sigma^2(F) + 0.0005F^2$ which led to a featureless analysis of variance in terms of $\sin\theta$ and F_o , max. $\Delta/\sigma = 0.03$, max. and min. height in final $\Delta\rho$ map 0.34 and -0.35 e \AA^{-3} , respectively.

Table 2. Bond lengths (\AA) and angles ($^\circ$)

N(1)–C(2)	1.377 (8)	N(1)–C(13)	1.381 (8)
C(2)–C(3)	1.497 (9)	C(2)–C(7)	1.360 (8)
C(3)–N(4)	1.504 (8)	C(3)–C(14)	1.521 (8)
N(4)–C(5)	1.511 (7)	N(4)–C(21)	1.494 (8)
C(5)–C(6)	1.529 (9)	C(6)–C(7)	1.491 (8)
C(7)–C(8)	1.434 (8)	C(8)–C(9)	1.391 (9)
C(8)–C(13)	1.414 (8)	C(9)–C(10)	1.378 (10)
C(10)–C(11)	1.396 (10)	C(11)–C(12)	1.384 (11)
C(12)–C(13)	1.394 (9)	O(12')–C(22)	1.244 (8)
C(14)–C(15)	1.523 (9)	C(15)–C(16)	1.528 (8)
C(15)–C(20)	1.544 (9)	C(16)–C(17)	1.381 (8)
C(16)–C(22)	1.404 (8)	C(17)–O(17')	1.272 (7)
C(17)–N(25)	1.419 (8)	C(19)–C(18x)	1.424 (16)
C(19)–C(18y)	1.216 (30)	C(19)–C(20)	1.564 (10)
C(20)–C(21)	1.514 (9)	C(22)–N(23)	1.412 (8)
N(23)–C(23')	1.459 (8)	N(23)–C(24)	1.363 (8)
C(24)–O(24')	1.231 (7)	C(24)–N(25)	1.367 (8)
C(25')–N(25)	1.458 (9)	C(2x)–O(1x)	1.370 (11)
C(2)–N(1)–C(13)	107.5 (5)	N(1)–C(2)–C(3)	123.2 (5)
N(1)–C(2)–C(7)	110.6 (5)	C(3)–C(2)–C(7)	126.2 (5)
C(2)–C(3)–N(4)	106.8 (4)	C(2)–C(3)–C(14)	114.7 (4)
N(4)–C(3)–C(14)	110.4 (4)	C(3)–N(4)–C(5)	111.0 (4)
C(3)–N(4)–C(21)	113.2 (4)	C(5)–N(4)–C(21)	113.5 (4)
N(4)–C(5)–C(6)	113.4 (4)	C(5)–C(6)–C(7)	110.4 (5)
C(2)–C(7)–C(8)	122.4 (5)	C(2)–C(7)–C(8)	107.3 (5)
C(6)–C(7)–C(8)	130.3 (5)	C(7)–C(8)–C(9)	135.1 (5)
C(7)–C(8)–C(13)	105.8 (5)	C(9)–C(8)–C(13)	119.1 (6)
C(8)–C(9)–C(10)	119.1 (6)	C(9)–C(10)–C(11)	121.3 (7)
C(10)–C(11)–C(12)	121.2 (7)	C(11)–C(12)–C(13)	117.4 (6)
N(1)–C(13)–C(8)	108.8 (5)	N(1)–C(13)–C(2)	129.2 (5)
C(8)–C(13)–C(2)	121.9 (6)	C(3)–C(14)–C(15)	112.8 (5)
C(14)–C(15)–C(16)	111.6 (4)	C(14)–C(15)–C(20)	106.8 (4)
C(16)–C(15)–C(20)	117.1 (5)	C(15)–C(16)–C(17)	121.8 (5)
C(15)–C(16)–C(22)	117.5 (5)	C(17)–C(16)–C(22)	120.5 (5)
C(16)–C(17)–O(17')	126.1 (5)	C(16)–C(17)–N(25)	118.0 (5)
O(17')–C(17)–N(25)	115.8 (5)	C(18x)–C(19)–C(18y)	104.7 (15)
C(18x)–C(19)–C(20)	120.5 (8)	C(18y)–C(19)–C(20)	121.7 (15)
C(19)–C(20)–C(21)	116.5 (5)	C(15)–C(20)–C(21)	107.8 (5)
C(19)–C(20)–C(22)	109.4 (5)	N(4)–C(21)–C(20)	113.0 (5)
O(12')–C(22)–C(16)	126.4 (5)	O(12')–C(22)–N(23)	116.2 (5)
C(16)–C(22)–N(23)	117.4 (5)	C(22)–N(23)–C(23')	119.4 (5)
C(22)–N(23)–C(24)	123.6 (5)	C(23')–N(23)–C(24)	116.9 (4)
N(23)–C(24)–O(24')	121.9 (5)	N(23)–C(24)–N(25)	116.9 (5)
O(24')–C(24)–N(25)	121.1 (6)	C(17)–N(25)–C(24)	122.7 (5)
C(17)–N(25)–C(25')	120.2 (5)	C(24)–N(25)–C(25')	117.0 (5)

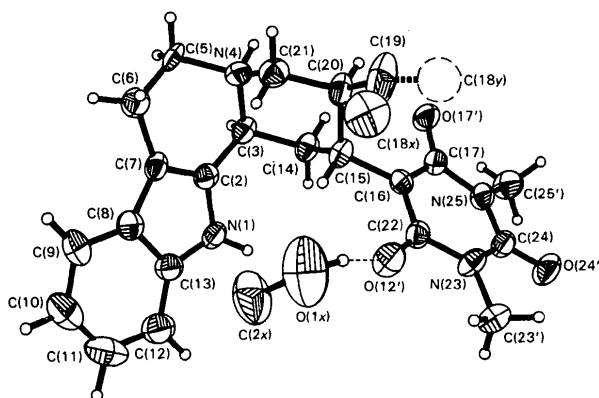


Fig. 1. The atom-numbering scheme.

Atomic scattering factors from *International Tables for X-ray Crystallography* (1974).

The main reason for the relatively high R index was probably the disordered ethyl group [$C(19)–C(18x)$ and $C(19)–C(18y)$, respectively]. The site-occupation factors for $C(18x)$ and $C(18y)$, respectively, were

initially refined [with their sum fixed at 1 and $U(C) = 0.1 \text{ \AA}^2$] and then fixed with the isotropic temperature factors allowed to refine. Atomic parameters are given in Table 1, selected bond distances and angles in Table 2.* Fig. 1 shows a thermal-ellipsoid plot with the atom numbering.

Related literature. For the preparation of the compound *via* a tandem-Knoevenagel-hetero-Diels-Alder reaction see Tietze, Bachmann & Schul (1988) and Tietze (1984). For structures of indoloquinolizine derivatives see Harms, Sheldrick, Schul & Tietze (1986) and Sawyer, Shariff & McLean (1985).

* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44975 (13 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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1,2,3,4-Tetrahydro-1,4-dimethylisoquinolinium Picrate

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Abstract. $C_{11}H_{16}N^+ \cdot C_6H_2N_3O_7^-$, $M_r = 390.36$, monoclinic, $P2_1/n$, $a = 13.266$ (3), $b = 8.127$ (2), $c = 16.744$ (4) Å, $\beta = 92.00$ (2)°, $V = 1804.1$ (7) Å³, $Z = 4$, $D_x = 1.44$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.71073$ Å, $\mu = 1.06$ cm⁻¹, $F(000) = 816$, $T = 293$ K, $R = 0.0560$ for 1537 reflections. The six-membered heterocyclic ring of the isoquinoline cation is in a half-chair conformation with *syn*-methyl groups at C(1) and C(4) occupying pseudo-axial and equatorial positions, respectively. The relevant torsion angles are C(10)C(9)C(1)CH₃ = -104.8 (3) and C(9)C(10)C(4)CH₃ = 139.9 (3)°. A nitrogen proton [H(2a'), \bar{x} , 1-y, 1-z] from the heterocyclic ring forms a bifurcated hydrogen bond to the phenolic O atom [N(2')...O(13) = 3.130 (4) Å] and to a nitro group O atom [N(2')...O(14a) = 2.943 (4) Å] of an adjacent picrate ion. The 1,2,3,4-tetrahydro-1,4-dimethylisoquinoline molecule is the result of an unusual, highly stereoselective alkylation of a boron-activated enamine.

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Experimental. Yellow, transparent crystal of dimensions 0.25 × 0.50 × 1.00 mm; Nicolet R3m/μ update of P2₁ diffractometer; data collected in Wyckoff mode (3 ≤ 2θ ≤ 45°, 2θ fixed, ω varied), scan rate 4–29.3° min⁻¹, graphite-monochromated Mo Kα radiation; lattice parameters from a least-squares refinement of 23 reflections (26.81 ≤ 2θ ≤ 42.85°), angles measured by a centering routine; systematic absences (h0l, h + l = 2n + 1, 0k0, k = 2n + 1) and Laue symmetry 2/m consistent with space group P2₁/n; monitored reflections 110 and $\bar{1}3\bar{1}$ showed only statistical variations in intensities; 1562 independent reflections measured (-14 ≤ h ≤ 14, 0 ≤ k ≤ 8, 0 ≤ l ≤ 18); 1537 ≥ 3σ(I); Lorentz-polarization corrections, ψ-scan empirical absorption correction (transmission factors 0.902–0.930); structure solved by direct methods, block-cascade least-squares refinement, H-atom positional parameters refined, single refined isotropic temperature factor; final R = 0.0560, wR = 0.0301 for 308 parameters and 1537 reflections, S = 1.519, (Δ/σ)_{max} = 0.028, (Δ/σ)_{av} = 0.007; largest peaks in the final difference map of 0.20 and -0.20 e Å⁻³, $\sum w(|F_o| - |F_c|)^2$ minimized with w =