

−0.754 (4) and −0.683 (4) Å respectively whereas N3 is displaced by −1.499 (3) Å out of this plane. The endocyclic bond lengths clearly indicate double bonds at N1—C2, 1.274 (3), and N4—C5, 1.286 (2) Å. In the dimethylamino moiety the N51 atom has essentially sp^3 -hybridized character [N51 lies some −0.332 (2) Å out of the plane through C5, C52 and C53], and the C5—N51 bond length, 1.394 (2) Å, is appreciably longer than the corresponding distance in (IVa). Steric hindrance is minimized by the dimethylamino moiety twisting away from the main plane through the molecule; the dihedral angle between the planes through C5, C5a, C9a and N1, and C5, C52 and C53 is 65.44 (1)°. The phenyl ring at C2 is planar within experimental error and makes a dihedral angle of 28.2 (1)° with the plane defined by N1, C2 and N3 in order to minimize the non-bonded contact between the H atom bonded to N3 and the *ortho*-H atom on the phenyl ring. The remaining aromatic ring, atoms C5a, C6, C7, C8, C9 and C9a, is not strictly planar, the largest deviation being 0.014 (2) Å for C9; the displacements of the 7- and 9-methyl substituents are 0.046 (4) and 0.062 (4) Å respectively. In the crystal structure, Fig. 2(b), the molecules pack so that a network of intermolecular hydrogen bonds is formed between pairs of N1 and N3 atoms, *viz.* N1⋯N3($x, \frac{1}{2} - y, -\frac{1}{2} + z$) and N3⋯N1($x, \frac{1}{2} - y, \frac{1}{2} + z$), 3.096 (3) Å.

All the figures were drawn using *PLUTO78* (Motherwell & Clegg, 1978), as modified by Dr A. Quick to run on the Amdahl computer at the University of London Computer Centre.

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Structure of Ethyl 5-Ethoxy-3-phenyl-2-indolecarboxylate

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Abstract. C₁₉H₁₉NO₃, $M_r = 309.37$, monoclinic, $P2_1/c$, $a = 10.322$ (3), $b = 21.063$ (5), $c = 15.006$ (5) Å, $\beta = 92.93$ (3)°, $V = 3258.22$ (1) Å³, $Z = 8$, $D_m = 1.27$ (5), $D_x = 1.26$ Mg m^{−3}, $\lambda(\text{Cu K}\alpha) = 1.5418$ Å, $\mu = 0.61$ mm^{−1}, $F(000) = 1312$, $T = 300$ K, final $R = 0.048$ for 4361 observed reflections. Two independent molecules per asymmetric unit. The phenyl ring connected to the planar indole rings is rotated out of the indole plane by 44.7 (4)° in molecule *A* and 47.3 (5)° in molecule *B*. The ethoxy-

carbonyl group makes an angle of 4.4 (6)° with the mean plane of the indole rings in molecule *A* and 14.7 (5)° in molecule *B*. The molecules in the asymmetric unit are held together by N—H⋯O bonds.

Introduction. Indole derivatives are important pharmacologically, possessing anti-allergic, central nervous system depressant and muscle relaxant properties (Harris & Uhle, 1960; Wei & Stanley,

1970; Reynolds & Carson, 1970; Houlihah, 1973; White & Black, 1976; Ho, Haegman & Prisco, 1986). The title compound having a $-\text{COOC}_2\text{H}_5$ group next to the indole N atom serves as the most versatile starting material to synthesize fused indole heterocycles of biological importance. The crystallographic study of the title compound was undertaken to establish the structure unambiguously, as very little information is available on non-steroidal indole derivatives (Chakraborty & Talapatra, 1986). This work forms part of the investigations of some pharmacologically important indoles and their precursors. The compound was synthesized by Fischer indolization (Huges, Lions, McKean, Murry, Callanan, Freeman, Ralph, Rassack, Dornbroski, Finch, Andrews, Betty, Scott, Vernon, Flack & Lawrence, 1938) of ethyl pyruvate-*p*-ethoxyphenyl-hydrazone using dry HCl gas.

Experimental. Transparent yellow crystals grown by diffusion of hexane in benzene solution; crystal of size $0.4 \times 0.2 \times 0.2$ mm mounted on Enraf-Nonius CAD-4 diffractometer; $\omega/2\theta$ scan; cell dimensions from least-squares refinement of 13 centered reflections in the range $10 \leq \theta \leq 30^\circ$; density by flotation technique; intensity data using Cu $K\alpha$ radiation to a maximum $2\theta = 130^\circ$; three standard reflections (160, 2, 1, 12, 319) monitored after every 2 h; 4868 independent reflections of which 4361 with $I \geq 3\sigma(I)$ considered observed; data corrected for Lorentz-polarization effects, an empirical absorption correction based on a series of ψ scans applied, minimum correction factor 0.972, maximum correction factor 0.999 and average correction factor 0.986. The structure was solved by *MULTAN80* (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980); all H atoms located from successive difference Fourier maps; full-matrix least-squares refinement with anisotropic thermal parameters for non-H atoms and isotropic thermal parameters for H atoms using *SHELX76* (Sheldrick, 1976). Final $R = 0.048$ and $wR = 0.054$, $w = K[\sigma^2(F) + |g|F^2]^{-1}$, $K = 7.944$, $g = 0.00047$, σ 's based on counting statistics; refinement terminated when shift/e.s.d. for non-H atoms was less than 0.2; the minimum and maximum residual electron densities in the final difference Fourier map were -0.25 and $0.21 \text{ e } \text{\AA}^{-3}$. Atomic scattering factors from *SHELX76*.

Discussion. The final positional parameters of non-H atoms with U_{eq} values are given in Table 1.* A

* 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 52757 (29 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Fractional coordinates ($\times 10^4$) and equivalent isotropic temperature factors ($\text{\AA}^2 \times 10^4$) for non-H atoms with e.s.d.'s in parentheses

$$U_{\text{eq}} = (1/3) \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	x	y	z	U_{eq}
N(1)	1186 (1)	-112 (1)	5837 (1)	475 (5)
C(2)	1076 (2)	-727 (1)	5550 (1)	444 (5)
C(3)	145 (2)	-1042 (1)	6025 (1)	430 (5)
C(4)	-1284 (2)	-597 (1)	7268 (1)	485 (6)
C(5)	-1491 (2)	-60 (1)	7757 (1)	494 (5)
C(6)	-777 (2)	504 (1)	7623 (1)	545 (6)
C(7)	125 (2)	536 (1)	6994 (1)	533 (6)
C(8)	354 (2)	-12 (1)	6496 (1)	456 (5)
C(9)	-328 (2)	-577 (1)	6630 (1)	451 (5)
C(10)	-248 (2)	-1718 (1)	6010 (1)	465 (6)
C(11)	-374 (2)	-2046 (1)	5228 (1)	575 (6)
C(12)	-919 (2)	-2682 (1)	5250 (2)	730 (9)
C(13)	-961 (2)	-3003 (1)	6045 (2)	800 (10)
C(14)	-669 (2)	-2683 (1)	6824 (2)	751 (9)
C(15)	-314 (2)	-2046 (1)	6815 (1)	595 (7)
O(16)	-2365 (1)	-12 (1)	8416 (1)	607 (5)
C(17)	-3034 (2)	-577 (1)	8644 (1)	597 (7)
C(18)	-3865 (3)	-423 (1)	9407 (2)	795 (9)
C(19)	1956 (2)	-915 (1)	4860 (1)	459 (5)
O(20)	2781 (1)	-567 (1)	4588 (1)	603 (4)
O(21)	1779 (1)	-1504 (1)	4568 (1)	533 (4)
C(22)	2636 (2)	-1721 (1)	3894 (1)	611 (7)
C(23)	2295 (3)	-2388 (1)	3693 (2)	942 (11)
N(1')	4195 (2)	525 (1)	4236 (1)	505 (5)
C(2')	4288 (2)	1153 (1)	4468 (1)	452 (5)
C(3')	5134 (2)	1460 (1)	3919 (1)	418 (4)
C(4')	6452 (2)	985 (1)	2629 (1)	472 (5)
C(5')	6680 (2)	422 (1)	2198 (1)	513 (6)
C(6')	6063 (2)	-149 (1)	2443 (1)	594 (7)
C(7')	5211 (2)	-161 (1)	3108 (1)	569 (6)
C(8')	4978 (2)	407 (1)	3553 (1)	483 (6)
C(9')	5596 (2)	979 (1)	3333 (1)	436 (5)
C(10')	5466 (2)	2140 (1)	3891 (1)	412 (5)
C(11')	4514 (2)	2606 (1)	3924 (1)	524 (6)
C(12')	4821 (2)	3242 (1)	3872 (1)	658 (8)
C(13')	6091 (3)	3431 (1)	3784 (1)	736 (9)
C(14')	7044 (2)	2976 (1)	3751 (1)	652 (8)
C(15')	6744 (2)	2338 (1)	3802 (1)	502 (6)
O(16')	7491 (1)	347 (1)	1509 (1)	637 (5)
C(17')	8135 (2)	894 (1)	1207 (1)	666 (7)
C(18')	9010 (3)	699 (1)	486 (2)	818 (9)
C(19')	3602 (2)	1341 (1)	5258 (1)	468 (5)
O(20')	2789 (1)	1018 (1)	5590 (1)	609 (5)
O(21')	4005 (1)	1895 (1)	5600 (1)	560 (4)
C(22')	3454 (2)	2095 (1)	6419 (1)	666 (7)
C(23')	3843 (3)	2762 (1)	6585 (2)	860 (10)

perspective view of the molecule with bond lengths and angles is shown in Fig. 1 and the *ORTEP* (Johnson, 1965) plot of one of the molecules with 50% probability thermal ellipsoids is shown in Fig. 2. The indole ring system is planar in both the molecules with a maximum deviation of 0.018 (2) \AA in molecule *A* and 0.010 (2) \AA in molecule *B*. The phenyl ring connected to the indole moiety is rotated through 44.7 (4) $^\circ$ in molecule *A* and 47.3 (5) $^\circ$ in molecule *B* out of the indole plane. The mean plane of the ethoxycarbonyl group is inclined to the indole rings at an angle of 4.4 (6) $^\circ$ in molecule *A* and 14.7 (7) $^\circ$ in molecule *B*. The ester moiety is *syn* to C=O about the C—O bond, the torsion angle C(22)—O(21)—C(19)—O(20) is 0.22 (5) $^\circ$ in molecule *A* and 2.10 (5) $^\circ$ in molecule *B*.

The bond lengths and angles in the two phenyl rings are normal. The two C—N bonds in the five-membered ring are almost equal having an average value of 1.364 (2) \AA . The bond length C(3)—C(9) =

1.439 (2) Å is longer than the normal aromatic C—C bond and agrees with the values observed in other indole derivatives (Chandrashekar & Pattabhi, 1980). The bond length C(2)—C(3) = 1.393 (2) Å is comparable with the standard aromatic C—C bond but is longer than the values observed in various other non-steroidal indole derivatives (Falkenberg & Carlstrom, 1971; Vijayalakshmi & Srinivasan, 1975; Sakaki, Sogo, Wakahara, Kanai, Fujiwara & Tomita, 1976; Ishida, Inoue & Tomita, 1979; Acheson, Wallis & Watkin, 1980; Chandrashekar & Pattabhi, 1980; Shoja, 1988). The bond angle C(4)—C(5)—O(16) is larger than C(6)—C(5)—O(16) by 11° and this may be due to the *cis* orientation of C(4)—C(5) and C(17)—O(16) about the C(5)—O(16)

bond causing the bond angle to be larger due to the repulsion between C(4) and C(17) (Sakaki *et al.*, 1976).

The C=O distances are normal. The apparent change in the bond lengths of the ethyl groups might be due to strong thermal vibrations of the terminal C atoms.

The molecular packing viewed down *a* is shown in Fig. 3. The molecules in the asymmetric unit are linked through N—H···O bonds [N···O 2.933 (3), 2.788 (3) Å, N—H···O 159.2 (7), 160.1 (6)°]. There is also an intramolecular H bond between N(1) and O(20) [N(1)···O(20) 2.731 (3), 2.760 (3) Å and N—H···O 88.72 (7), 89.54 (6)°]. In addition, there are a few intermolecular contacts less than 3.4 Å.

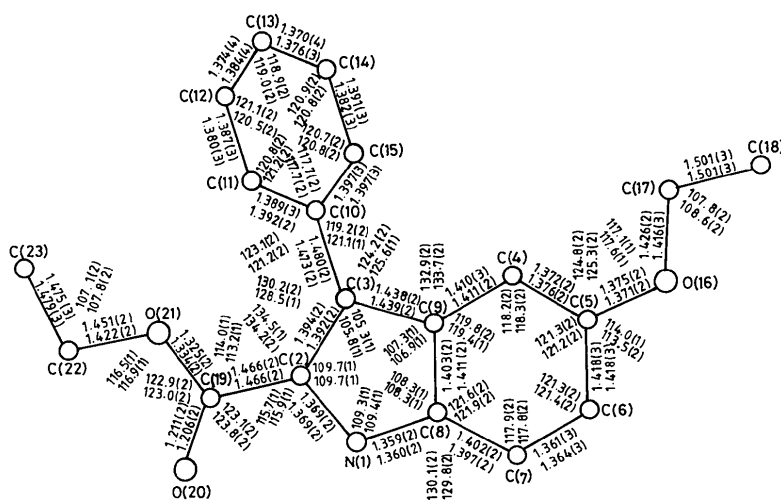


Fig. 1. A perspective view of the molecule with bond lengths (Å) and angles (°) for molecules *A* and *B*.

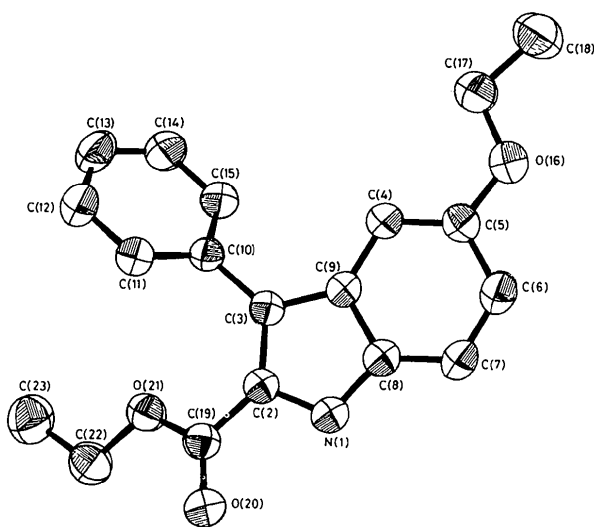


Fig. 2. ORTEP plot of one of the molecules with 50% probability thermal ellipsoids.

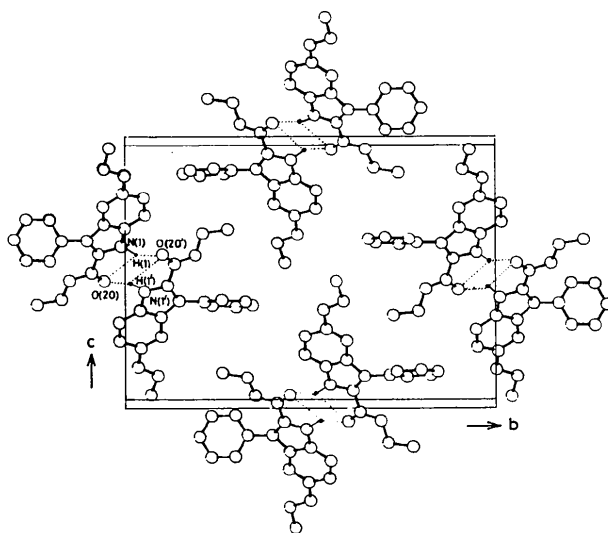


Fig. 3. A partial view of the molecular packing down *a*. Dotted lines indicate hydrogen bonding.

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Structure of 5 β -Dihydrotestosterone

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Abstract. 17 β -Hydroxy-5 β -androstan-3-one, C₁₉H₃₀O₂, M_r = 290.45, orthorhombic, $P2_12_12_1$, a = 11.7821 (6), b = 21.2184 (8), c = 6.5322 (2) Å, V = 1633.0 (2) Å³, Z = 4, D_x = 1.181 Mg m⁻³, λ (Cu $K\alpha$) = 1.54178 Å, μ = 0.58 mm⁻¹, $F(000)$ = 640, T = 293 K, R = 0.033 for 1849 unique observed reflections. The molecular conformation of 5 β -dihydrotestosterone shows the strong bending typical of 5 β -steroids: the bowing angle of the A ring, relative to the remainder of the steroid, is 65.1°. Bowing shortens the distance between the terminal O atoms, O(3) and O(17), to 9.824 (2) Å which is *ca* 1 Å shorter than was observed in 5 α -dihydrotestosterone and testosterone. The effects of both the bowing and the shorter separation between O(3) and O(17) may explain a difference in the affinity of 5 β -dihydrotestosterone for the dexamethasone binding site on membranes compared to that of the other two com-

pounds. A unique conformational feature of 5 β -dihydrotestosterone is the flattening of the A ring on the side containing the C(3)—C(4) bond; this may be due to the combination of the 3-oxo substitution and the 5 β -configuration.

Introduction. Dexamethasone binding sites have been identified on both nuclear envelopes and plasma membranes (Howell & Lefebvre, 1989; Howell, Po & Lefebvre, 1989) and are postulated to be important in the transport of hormones. Our study of the activity profile of steroids that interact with the dexamethasone binding sites has shown that steroid affinity for these sites is strongly correlated to the distance between the terminal O atoms of the steroid (Roszak, Coddling & Lefebvre, 1990). Analysis of the crystal structures of pregnanes showed that the distance between the O atoms, O(3) and O(20), is consistently in the range 11.2–11.9 Å whereas, for testosterone, the distances between the terminal O atoms, O(3) and O(17 β), are 10.94 and 10.93 Å in the two independent molecules of testosterone

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