C2—O1—C5	105.41 (13)	C2*A*—C1*A*—C6*A*	116.6 (2)
C2—N3—C4	105.21 (14)	C2*A*—C1*A*—C2	123.03 (15)
N3—C2—O1	115.49 (15)	C6*A*—C1*A*—C2	120.3 (2)
N3—C2—C1*A*	127.5 (2)	C5*A*—C6*A*—C1*A*	121.0 (2)
O1—C2—C1*A*	116.96 (14)	O5—C5—O1	120.2 (2)
O2*B*—N2—O2*A*	124.5 (2)	O5—C5—C4	135.5 (2)
O2*B*—N2—C2*A*	117.8 (2)	O1—C5—C4	104.35 (14)
O2*A*—N2—C2*A*	117.7 (2)	C6—C4—N3	128.9 (2)
C6—N4—C8	123.16 (15)	C6—C4—C5	121.5 (2)
C6—N4—C7	120.2 (2)	N3—C4—C5	109.54 (15)
C8—N4—C7	116.6 (2)	N4—C6—C4	129.3 (2)
C3*A*—C2*A*—C1*A*	122.8 (2)	C2*A*—C3*A*—C4*A*	118.9 (2)
C3*A*—C2*A*—N2	116.2 (2)	C5*A*—C4*A*—C3*A*	120.0 (2)
C1*A*—C2*A*—N2	120.93 (14)	C4*A*—C5*A*—C6*A*	120.6 (2)

C4—N3—C2—O1	0.2 (2)
C4—N3—C2—C1*A*	−179.3 (2)
C5—O1—C2—N3	0.1 (2)
O2*B*—N2—C2*A*—C3*A*	70.3 (2)
O2*A*—N2—C2*A*—C3*A*	−106.4 (2)
O2*B*—N2—C2*A*—C1*A*	−112.3 (2)
O2*A*—N2—C2*A*—C1*A*	71.0 (2)
N2—C2*A*—C1*A*—C2	6.0 (3)
N3—C2—C1*A*—C2*A*	12.2 (3)
C2—O1—C5—O5	−179.7 (2)
C2—O1—C5—C4	−0.4 (2)
C2—N3—C4—C6	175.9 (2)
C2—N3—C4—C5	−0.4 (2)
O5—C5—C4—C6	3.0 (3)
O1—C5—C4—C6	−176.19 (15)
O5—C5—C4—N3	179.6 (2)
O1—C5—C4—N3	0.5 (2)
C8—N4—C6—C4	0.2 (3)
C7—N4—C6—C4	−177.9 (2)
N3—C4—C6—N4	0.2 (3)
C5—C4—C6—N4	176.2 (2)
C1*A*—C2*A*—C3*A*—C4*A*	−3.1 (3)
N2—C2*A*—C3*A*—C4*A*	174.3 (2)
C2*A*—C3*A*—C4*A*—C5*A*	1.2 (3)
C3*A*—C4*A*—C5*A*—C6*A*	1.6 (3)
C1*A*—C6*A*—C5*A*—C4*A*	−2.7 (3)

All non-H atoms were refined with anisotropic displacement parameters. All H atoms were placed in fixed positions.

Data collection: Rigaku AFC software. Cell refinement: Rigaku AFC software. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1995). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ZORTEP* (Zsolnai, 1997). Software used to prepare material for publication: *SHELXL*93. Geometric calculations: *PARST* (Nardelli, 1983).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: DE1078). Services for accessing these data are described at the back of the journal.

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Ethyl 5-Ethoxy-3-methyl-1*H*-indole-2-carboxylate

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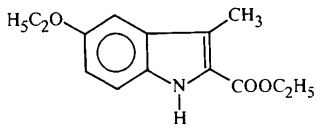
Abstract

The title compound, $C_{14}H_{17}NO_3$, having an ethoxycarbonyl group at C2, serves as an important precursor in the synthesis of fused-indole heterocycles of biological importance. The indole moiety is planar and it forms dihedral angles of 2.3 (1) and 3.9 (1)° with the ethoxycarbonyl group at C2 and the ethoxy group at C5, respectively. The centrosymmetrically related molecules are held together by hydrogen bonds across a centre of symmetry and form dimers.

Comment

Indole derivatives have important pharmacological uses because of the range of anti-allergic, central nervous system depressant and muscle relaxant properties (Harris & Uhle, 1960; Wei & Stanley, 1970; Reynolds & Carson, 1970; Ho *et al.*, 1986).

The indole ring of the title compound, (I), is planar, with a maximum deviation of 0.007 (5) Å from the best plane. The ethoxy group at C5 and the ethoxycarbonyl group at C2 are inclined with respect to the mean plane of indole at angles of 3.9 (1) and 2.3 (1)°, respectively. The methyl group at C3 is in the plane of the indole moiety, with a deviation of 0.018 (2) Å.



(I)

The *cis* orientation of O16—C17 with respect to C4—C5 about the C5—O16 bond results in repulsion between the C4 and C17 atoms and because of this the bond angle C4—C5—O16 is increased by about 10° compared with C6—C5—O16 (Sakaki *et al.*, 1976). The torsion angle C4—C5—O16—C17 is −2.7 (2)°.

The centrosymmetrically related molecules are held together by hydrogen bonds across a centre of symmetry and form dimers [N1—H1···O11^{i} 2.852 (2), H1···O11^{i} 1.83 (2), N1—H1 1.09 (2) Å and N1—H1···O11^{i} 153 (1)°; symmetry code: (i) $-x$, $2-y$, $1-z$]. In addition, the H1 atom is under the active influence of O11 of the same molecule [H1···O11 2.63 (2) Å] and this may be the reason why the intermolecular hydrogen bond between H1 and O11^{i} deviates from linearity by about 27°.

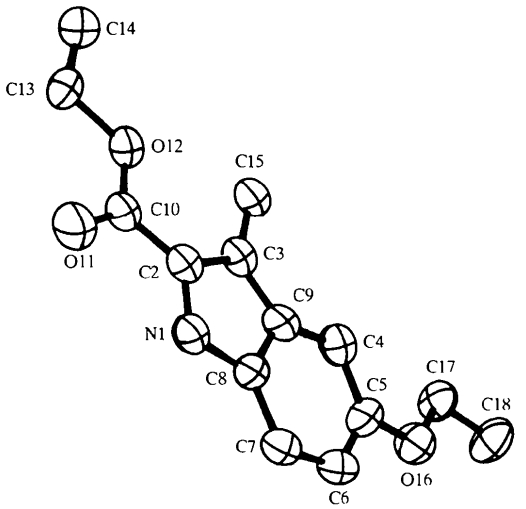


Fig. 1. *ORTEP* (Johnson, 1965) plot of the title molecule with 60% probability displacement ellipsoids.

Experimental

The title compound, (I), was synthesized by Fisher indolization (Huges *et al.*, 1938) using ethyl 2-oxo-butanoate and *p*-ethoxyphenylhydrazine in the presence of dry hydrogen chloride gas.

Crystal data

$C_{14}H_{17}NO_3$
M_r = 247.29
Cu $K\alpha$ radiation
λ = 1.5418 Å
Triclinic
$P\bar{1}$
a = 7.855 (2) Å
b = 8.669 (1) Å
c = 11.115 (2) Å
α = 70.38 (1)°
β = 69.39 (1)°
γ = 73.97 (1)°
V = 656.5 (2) Å^3
Z = 2
D_x = 1.251 Mg m^{-3}
D_m = 1.270 Mg m^{-3}
D_m measured by flotation in potassium iodide and water
Cell parameters from 25 reflections
θ = 10–50°
μ = 0.717 mm^{-1}
T = 293 (2) K
Plate
0.40 × 0.30 × 0.15 mm
Yellow

Data collection

Enraf–Nonius CAD-4 diffractometer
ω–2θ scans
Absorption correction: none
2341 measured reflections
2341 independent reflections
1995 reflections with $F^2 > 2\sigma(F^2)$
θ_{max} = 69.76°
$h = -8 \rightarrow 7$
$k = 0 \rightarrow 10$
$l = -12 \rightarrow 13$
3 standard reflections every 70 reflections
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.045
$wR(F^2)$ = 0.160
S = 1.084
2291 reflections
215 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.0964P)^2 + 0.0227P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.201 e Å^{-3}
$\Delta\rho_{min}$ = −0.161 e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

N1—C8	1.363 (2)	C6—C7	1.367 (2)
N1—C2	1.383 (2)	C7—C8	1.407 (2)
C2—C3	1.381 (2)	C8—C9	1.403 (2)
C2—C10	1.462 (2)	C10—O11	1.214 (2)
C3—C9	1.427 (2)	C10—O12	1.328 (2)
C3—C15	1.491 (2)	O12—C13	1.450 (2)
C4—C5	1.382 (2)	C13—C14	1.492 (2)
C4—C9	1.408 (2)	O16—C17	1.421 (2)
C5—O16	1.374 (2)	C17—C18	1.504 (2)
C5—C6	1.415 (2)		
C8—N1—C2	108.23 (12)	N1—C8—C9	108.59 (12)
C3—C2—N1	109.89 (12)	N1—C8—C7	130.35 (14)
C3—C2—C10	131.87 (12)	C9—C8—C7	121.05 (14)
N1—C2—C10	118.24 (12)	C8—C9—C4	120.78 (13)
C2—C3—C9	105.98 (12)	C8—C9—C3	107.31 (12)
C2—C3—C15	129.15 (13)	C4—C9—C3	131.90 (13)
C9—C3—C15	124.86 (13)	O11—C10—O12	123.18 (13)
C5—C4—C9	117.66 (14)	O11—C10—C2	123.90 (13)
O16—C5—C4	124.42 (14)	O12—C10—C2	112.91 (12)
O16—C5—C6	114.64 (12)	C10—O12—C13	117.16 (11)
C4—C5—C6	120.94 (14)	O12—C13—C14	107.11 (14)
C7—C6—C5	121.92 (13)	C5—O16—C17	117.80 (12)
C6—C7—C8	117.64 (14)	O16—C17—C18	107.5 (2)

The atomic coordinates of the non-H atoms were refined with anisotropic displacement parameters using *SHELXL*93 (Sheldrick, 1993). All the planar H atoms were located from difference Fourier maps, while the ethyl and methyl

H atoms were fixed based on geometrical considerations and refined with isotropic displacement parameters. Normally, absorption corrections would have been applied, but because only light atoms are present in the structure and the value of μ reasonable, the intensity data were not corrected for absorption.

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989). Data reduction: *DATRD2* in *NRCVAX* (Gabe *et al.*, 1989). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL93*. Molecular graphics: *ORTEP* (Johnson, 1965). Software used to prepare material for publication: *SHELXL93*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: DE1073). Services for accessing these data are described at the back of the journal.

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1,5-Dinitro-1*H*-indazole

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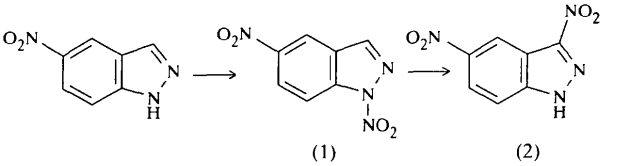
Abstract

The title compound, $C_7H_4N_4O_4$, was obtained by nitration of 5-nitro-1*H*-indazole. It has a planar indazole ring, with the N1-bound nitro group almost coplanar with the ring [twist angle 3.9 (2)°], while the C5-bound nitro group is twisted by 19.2 (2)° out of the plane of the molecule. The molecules in the crystal structure are arranged in planes. They are connected to each other by weak C—H···O hydrogen bonds, with C···O distances of 3.276 (3) Å.

Comment

N-Nitroazoles can be considered as derivatives of nitramide (NH_2NO_2), as well as nitramine, *e.g.* *N*-methyl-*N*-phenylnitramine. In the first case, the nitramide residue forms part of the heteroaromatic system, while in true nitramines, it is bonded to the aromatic (phenyl, naphthyl) or heteroaromatic (pyridyl, thiazolyl) system. In spite of this difference, both classes of *N*-nitro compounds have a common feature, *i.e.* under the influence of an acid or elevated temperature, the nitro group migrates from N to the aromatic C atom. *N*-Methyl-*N*-pyridylnitramine gives a mixture of 3-nitro- and 5-nitro-2-methylaminopyridine (Daszkiewicz *et al.*, 1977), while 9-nitrocarbazole rearranges to 1-nitro- and 3-nitrocarbazole (Kyzioł & Daszkiewicz, 1985). There is a general rule that the nitro group is shifted three or five nodes from the migration origin. There is only one exception; it was claimed that derivatives of 2-nitroindazole containing an additional nitro group bonded to the benzene ring rearranged in boiling anisole to the corresponding 3-nitroindazole derivatives (Cohen-Fernandes & Habraken, 1971). However, the spectral data of the *N*-nitro compounds do not allow 1-nitro and 2-nitroindazole to be distinguished. Moreover, these compounds were obtained by nitration with the mixed anhydride HNO_3–Ac_2O. Under these conditions, structurally related benzotriazole forms 1-nitrobenzotriazole (Cohen-Fernandes & Habraken, 1971). This prompted us to examine one of the aforementioned *N*-nitroindazoles. The results presented below show that nitration of 5-nitroindazole gives 1,5-dinitroindazole, (1).



(1) (2)

N-Nitroazoles have not been as frequently studied as secondary nitramines, but the structures of 1-nitropyrazole [(3); Tarımcı & Schempp, 1977], 1,4-dinitroimidazole [(4); Grimmet *et al.*, 1989] and 1-nitro-3-azo-1,2,4-triazole [(5); Cromer *et al.*, 1988] were determined. All the molecules are planar, the torsion angle along the N—NO_2 bond varies from 1.8 (2)° in (3) to 9.4 (2)° in (4). The N—NO_2 bond is longer [1.42 (2) Å] than in aromatic nitramines (1.35 Å), while the C—N bond is