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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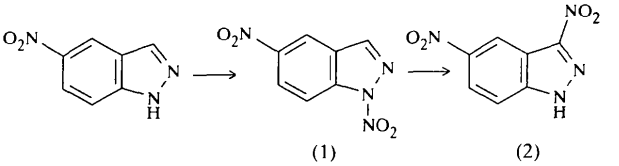
Abstract

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

shorter [1.36 (1) *versus* 1.42 Å; Anulewicz *et al.*, 1993; Ejsmont *et al.*, 1998]. This suggests that the NNO_2 group forms a conjugated π-electron system with the aromatic ring. In 1,5-dinitroindazole (Fig. 1), the nitro group at N1 is practically coplanar with the plane of the indazole ring [twist angle 3.9 (2)°], while the C3-bound nitro group is twisted by 19.2 (2)° out of the ring. This twist is probably caused by a weak C—H···O hydrogen bond, with an intermolecular C···O distance of 3.276 (3) Å.

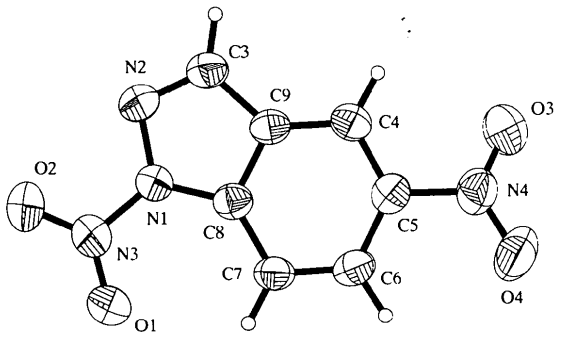


Fig. 1. The molecular structure of 1,5-dinitroindazole showing 50% probability displacement ellipsoids.

The geometry of the six-membered ring of the indazole molecule is deformed similar to the situation found in 3,5-dinitroindazole (Gzella & Wrzeciono, 1991), with shorter C4—C5 and C6—C7 bonds, smaller C9—C4—C5 and C6—C7—C8 angles, and larger C4—C5—C6 and C7—C8—C9 angles; this is probably the result of the interaction of the strongly electronegative NO_2 group with the ring. The C5—N4 bond length of 1.465 (3) Å is typical of a C_{ar}—NO_2 single bond, while the N1—N3 bond length [1.393 (2) Å] is similar to that found in *N*-nitroazoles, but longer than in typical nitramines.

Comparing the geometry of the pyrazole ring in (1) with that of 3,5-dinitroindazole, (2), one should note that the N2—C3 bond length in (1) is 0.04 Å shorter than the corresponding bond length in (2), while the N1—N2, N1—C8 and C3—C9 bond lengths are 0.02 (1) Å longer. This may indicate that delocalization of the charge within the pyrazole ring is easier when an NO_2 group is substituted at C3 rather than at the N1 position.

There is one independent 1,5-dinitroindazole molecule in the asymmetric unit. The molecules are arranged in planes and are connected to each other by weak C—H···O hydrogen bonds. They form layers separated by 3.38 (1) Å.

Experimental

We have applied a previously reported nitration procedure (Cohen-Fernandes & Habraken, 1971) to 5-nitroindazole and obtained *N*,5-dinitroindazole as white rods (m.p. 440–442 K, with rearrangement). Its spectral properties (IR and 1H NMR) are identical to those described by Cohen-Fernandes & Habraken (1971). Crystals suitable for X-ray diffraction studies were obtained by slow evaporation at room temperature from a methanol solution.

Crystal data

$C_7H_4N_4O_4$
M_r = 208.14
Monoclinic
$P2_1/n$
a = 7.631 (2) Å
b = 10.888 (2) Å
c = 9.917 (2) Å
β = 94.14 (3)°
V = 821.8 (3) Å^3
Z = 4
D_x = 1.682 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 19 reflections
θ = 8–12°
μ = 0.142 mm^{-1}
T = 293 (2) K
Irregular
0.6 × 0.4 × 0.4 mm
Colorless

Data collection

Kuma KM-4 diffractometer
ω–θ scans
Absorption correction: none
2888 measured reflections
1451 independent reflections
1234 reflections with $I > 2\sigma(I)$
R_{int} = 0.023

θ_{max} = 25.07°
h = −9 → 9
k = 0 → 12
l = −11 → 11
2 standard reflections
every 50 reflections
intensity decay: 0.86%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.041
$wR(F^2)$ = 0.117
S = 1.183
1451 reflections
136 parameters
H atoms: riding model
$w = 1/[\sigma^2(F_o^2) + (0.0462P)^2 + 0.2656P]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max}$ = 0.012
$\Delta\rho_{max}$ = 0.197 e Å^{-3}
$\Delta\rho_{min}$ = −0.149 e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

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

C3—N2	1.295 (3)	C8—N1	1.380 (2)
C3—C9	1.430 (3)	C8—C9	1.402 (3)
C4—C5	1.368 (3)	N1—N2	1.366 (2)
C4—C9	1.386 (3)	N1—N3	1.393 (2)
C5—C6	1.390 (3)	N3—O1	1.209 (2)
C5—N4	1.465 (3)	N3—O2	1.211 (2)
C6—C7	1.372 (3)	N4—O3	1.213 (3)
C7—C8	1.389 (3)	N4—O4	1.216 (2)
N2—C3—C9	112.74 (18)	C8—C9—C3	104.88 (18)
C5—C4—C9	116.39 (18)	N2—N1—C8	113.49 (15)
C4—C5—C6	123.50 (18)	N2—N1—N3	118.46 (16)
C4—C5—N4	118.07 (18)	C8—N1—N3	127.90 (16)
C6—C5—N4	118.41 (18)	C3—N2—N1	104.69 (16)
C7—C6—C5	120.83 (18)	O1—N3—O2	127.7 (2)
C6—C7—C8	116.45 (18)	O1—N3—N1	115.00 (18)
N1—C8—C7	133.38 (18)	O2—N3—N1	117.30 (18)
N1—C8—C9	104.17 (16)	O3—N4—O4	123.8 (2)
C7—C8—C9	122.44 (18)	O3—N4—C5	118.21 (18)
C4—C9—C8	120.38 (18)	O4—N4—C5	117.96 (19)
C4—C9—C3	134.74 (19)		

Cell refinement: *KM-4 Software* (Kuma, 1997). Data reduction: *KM-4 Software*. Program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990*a*). Program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997). Molecular graphics: *SHELXTL* (Sheldrick, 1990*b*). Software used to prepare material for publication: *SHELXL97*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: KA1282). Services for accessing these data are described at the back of the journal.

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2,3-Dihydrodioxin[2,3-*b*]acridin-11(6*H*)-one

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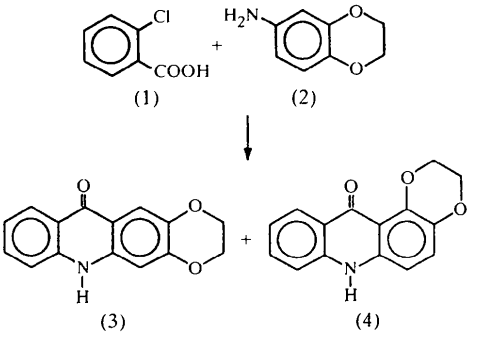
Abstract

The title compound, $C_{15}H_{11}NO_3$, belongs to a series of new potential antiviral agents against the herpes virus containing a fused ring system. The acridinone skeleton adopts a boat conformation, with greater folding at the junction with the dioxane ring. This ring is twisted with an approximate twofold axis bisecting the two C—C bonds.

Comment

This work has been undertaken in the context of our studies on acridine derivatives with potential pharmacological properties. Acridines are a well known group of antibacterial, antitumour and antifungal drugs (Babu *et al.*, 1986; Miyahara *et al.*, 1982; Crémieux *et al.*, 1994; Karolak-Wojciechowska *et al.*, 1996). Recently our attention has been focused on dioxanoacridinones obtained by condensing 2-chlorocarboxylic acid (1) and 1,4-benzodioxan-6-amine (2) (see scheme). According to



the Ullmann's reaction, two isomers can be obtained [(3) and (4)]. These dioxanoacridinones, (3) and (4), are under investigation as potential antiviral agents against the herpes virus (Mucsi *et al.*, 1997). With the aim of comparing the biological activity of the isomers with their structures, the title compound (3) has been the subject of an X-ray investigation. The choice of molecule (3) rather than (4) was based on crystal quality. The molecule of (3) is presented in Fig. 1 and therefore the structures of both isomers are confirmed.

Besides the confirmation of the chemical structure, some interesting structural observations in the geometry of the molecule of (3) can be made. The basic acridi-

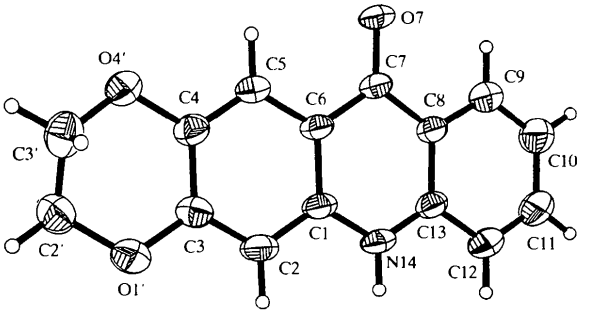


Fig. 1. Molecular structure of (3) showing 50% probability displacement ellipsoids.