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Structure of 1*H*-Indazole-3-carboxylic Acid

By Franco Benetollo

ICTR CNR, Corso Stati Uniti 4, 35020 *Padova, Italy*

and Antonio Del Pra

Istituto Chimico Farmaceutico e Tossicologico, Università di Milano, Viale Abruzzi 42, 20131 *Milano, Italy*

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Abstract. $C_8H_6N_2O_2$, $M_r = 162.15$, monoclinic, $P2_1/n$, $a = 10.402$ (2), $b = 15.025$ (3), $c = 9.467$ (2) Å, $\beta = 96.24$ (3)°, $V = 1470.8$ (5) Å^3, $Z = 8$, D_m(flotation in heptane/carbon tetrachloride) = 1.45, $D_x = 1.46$ Mg m^{-3}, λ(Mo $K\bar{\alpha}$) = 0.71069 Å, $\mu = 0.102$ mm^{-1}, $F(000) = 672$, $T = 295$ K, $R = 0.041$ ($wR = 0.048$) for the 2105 observed reflections with $I \geq 2.5\sigma(I)$. In both molecules of the asymmetric unit the carboxy group prefers a near coplanar [4.8 (1) and 5.4 (1)°] and *transoid* orientation with respect to the strictly planar heterocyclic ring. All bond lengths and valence angles correspond, within experimental e.s.d., to expected values. The two N atoms and the carboxy group of each molecule of the crystal are involved in an infinite three-dimensional O—H···N and N—H···O hydrogen-bond network, which is mainly responsible for the packing. All hydrogen-bond dimensions fall within the ranges of observed values.

Experimental. A prismatic white crystal of dimensions 0.70 × 0.48 × 0.40 mm was lodged in a Lindemann glass capillary and centred on a four-circle Philips PW1100 diffractometer with graphite-monochromated Mo $K\bar{\alpha}$ radiation. The orientation matrix and preliminary unit-cell dimensions were determined from 25 reflections found by mounting the crystal at random, varying each of the orientation angles χ and φ over a range of 120°, with $7 \leq \theta \leq 9°$. For the determination of precise lattice parameters, 25 strong reflections with $9 \leq \theta \leq 14°$ were considered. Integrated intensities for *hkl* reflections in the interval $h = \pm 12$, $k = 0 \rightarrow 17$, $l = 0 \rightarrow 11$, $\theta = 2$–25°, were measured using $\theta/2\theta$ scans, and two standard reflections, $\bar{4}62$ and 341, were measured every 180 min. There were no significant fluctuations of intensities other than those expected from Poisson statistics. In total, 2878 reflections were measured, of which 2595 were unique with 2105 being observed [$I \geq 2.5\sigma(I)$]. The intensity data were collected at room temperature and corrected for Lorenz–polarization effects but not for absorption.

The structure was solved by using direct methods (*SHELXS*86; Sheldrick, 1985) and refined with full-matrix least squares; anisotropic thermal parameters were assigned to all non-H atoms. H atoms were located by difference Fourier synthesis and refined isotropically. The function minimized was $\sum w\Delta^2$ where $\Delta = (|F_o| - |F_c|)$ and $w = [\sigma^2(F_o) + 0.004031(F_o)^2]^{-1}$. Final values were $R = 0.041$, $wR = 0.048$ and $S = 0.94$, for 265 parameters refined. $(\Delta/\sigma)_{\max} = 0.002$. The final difference Fourier map showed no unusual features ($\Delta\rho = -0.34 \rightarrow 0.16$ e Å^{-3}).

Data processing and computation were carried out using the *SHELX*76 program package (Sheldrick, 1976) with the atomic scattering factors taken from *International Tables for X-ray Crystallography* (1974, Vol. IV). Drawings were produced using *ORTEP*II (Johnson, 1976).

The atomic coordinates are listed in Table 1* and bond distances and angles are presented in Table 2; significant hydrogen-bonding geometries are given in Table 3. A view of the two molecules of the asymmetric unit, along with the numbering scheme, is shown in Fig. 1, and the crystal packing down **c** is depicted in Fig. 2 where the most significant hydrogen bonds (< 2.20 Å) are designated by dashed lines.

Related literature. Lonidamine (Doridamine, Angelini®), or 1-(2,4-dichlorobenzyl)-1*H*-indazole-3-carboxylic acid, and many of its derivatives (Baiocchi, Benetollo, Bombieri & Del Pra, 1989; Benetollo, Del Pra & Baiocchi, 1990), among which the title compound, have been considered as a part of our investigations on structure–activity relationships in anticancer agents.

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* Lists of structure factors, H-atom coordinates and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55699 (15 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: NA1014]

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Table 1. *Fractional coordinates and equivalent isotropic thermal parameters* ($Å^2 \times 10^3$)

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

	x	y	z	U_{eq}
O(1)	0.5006 (1)	0.4234 (1)	0.2232 (1)	41 (1)
O(2)	0.5198 (1)	0.3561 (1)	0.4364 (1)	40 (1)
N(1)	0.3009 (1)	0.3146 (1)	0.1272 (1)	34 (1)
N(2)	0.2032 (1)	0.2559 (1)	0.1143 (2)	35 (1)
C(1)	0.3579 (2)	0.3073 (1)	0.2603 (2)	30 (1)
C(2)	0.2949 (2)	0.2419 (1)	0.3359 (2)	31 (1)
C(3)	0.1940 (2)	0.2104 (1)	0.2377 (2)	32 (1)
C(4)	0.1057 (2)	0.1462 (1)	0.2740 (2)	38 (1)
C(5)	0.1234 (2)	0.1135 (1)	0.4108 (2)	43 (1)
C(6)	0.2247 (2)	0.1445 (1)	0.5104 (2)	45 (1)
C(7)	0.3098 (2)	0.2076 (1)	0.4764 (2)	38 (1)
C(8)	0.4673 (2)	0.3640 (1)	0.3147 (2)	31 (1)
N(11)	0.3022 (1)	0.4869 (1)	0.6346 (1)	36 (1)
N(21)	0.2771 (2)	0.5137 (1)	0.4979 (2)	39 (1)
O(21)	0.1479 (2)	0.3187 (1)	0.8157 (2)	62 (1)
O(11)	0.3042 (1)	0.4155 (1)	0.8914 (1)	50 (1)
C(11)	0.2163 (2)	0.4243 (1)	0.6544 (2)	34 (1)
C(21)	0.1312 (2)	0.4097 (1)	0.5277 (2)	34 (1)
C(31)	0.1746 (2)	0.4697 (1)	0.4282 (2)	36 (1)
C(41)	0.1158 (2)	0.4767 (1)	0.2880 (2)	45 (1)
C(51)	0.0126 (2)	0.4223 (1)	0.2517 (2)	50 (1)
C(61)	−0.0326 (2)	0.3620 (1)	0.3486 (2)	49 (1)
C(71)	0.0247 (2)	0.3544 (1)	0.2869 (2)	42 (1)
C(81)	0.2181 (2)	0.3802 (1)	0.7943 (2)	38 (1)

Table 2. *Bond lengths* (Å) *and angles* (°)

O(1)—C(8)	1.317 (2)	O(2)—C(8)	1.226 (2)
N(1)—N(2)	1.341 (2)	N(1)—C(1)	1.337 (2)
N(2)—C(3)	1.366 (2)	C(1)—C(2)	1.417 (2)
C(1)—C(8)	1.469 (2)	C(2)—C(3)	1.407 (2)
C(2)—C(7)	1.420 (2)	C(3)—C(4)	1.399 (3)
C(4)—C(5)	1.379 (3)	C(5)—C(6)	1.415 (3)
C(6)—C(7)	1.360 (3)	N(11)—N(21)	1.354 (2)
N(11)—C(11)	1.324 (2)	N(21)—C(31)	1.362 (2)
O(21)—C(81)	1.209 (3)	O(11)—C(81)	1.322 (2)
C(11)—C(21)	1.428 (2)	C(11)—C(81)	1.479 (3)
C(21)—C(31)	1.413 (3)	C(21)—C(71)	1.405 (3)
C(31)—C(41)	1.404 (3)	C(41)—C(51)	1.364 (3)
C(51)—C(61)	1.405 (3)	C(61)—C(71)	1.383 (3)

N(2)—N(1)—C(1)	106.6 (1)	N(1)—N(2)—C(3)	112.0 (2)
N(1)—C(1)—C(8)	122.0 (2)	N(1)—C(1)—C(2)	110.5 (2)
C(2)—C(1)—C(8)	127.4 (2)	C(1)—C(2)—C(7)	135.7 (2)
C(1)—C(2)—C(3)	104.7 (1)	C(3)—C(2)—C(7)	119.6 (2)
N(2)—C(3)—C(2)	106.2 (2)	C(2)—C(3)—C(4)	122.2 (2)
N(2)—C(3)—C(4)	131.6 (2)	C(3)—C(4)—C(5)	116.9 (2)
C(4)—C(5)—C(6)	121.5 (2)	C(5)—C(6)—C(7)	122.0 (2)
C(2)—C(7)—C(6)	117.9 (2)	O(2)—C(8)—C(1)	121.5 (2)
O(1)—C(8)—C(1)	114.3 (1)	O(1)—C(8)—O(2)	124.2 (2)
N(21)—N(11)—C(11)	106.5 (2)	N(11)—N(21)—C(31)	112.2 (2)
N(11)—C(11)—C(81)	120.1 (2)	N(11)—C(11)—C(21)	110.9 (2)
C(21)—C(11)—C(81)	129.0 (2)	C(11)—C(21)—C(71)	136.1 (2)
C(11)—C(21)—C(31)	104.4 (2)	C(31)—C(21)—C(71)	119.6 (2)
N(21)—C(31)—C(21)	106.1 (2)	C(21)—C(31)—C(41)	122.7 (2)
N(21)—C(31)—C(41)	131.2 (2)	C(31)—C(41)—C(51)	116.3 (2)
C(41)—C(51)—C(61)	122.2 (2)	C(51)—C(61)—C(71)	122.1 (2)
C(21)—C(71)—C(61)	117.2 (2)	O(11)—C(81)—C(11)	112.6 (2)
O(21)—C(81)—C(11)	122.9 (2)	O(21)—C(81)—O(11)	124.5 (2)

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

D—H···*A*	*D*···*A*	H···*A*	*D*—H···*A*
O(1)—H(1)···N(11^{i})	2.691 (2)	1.70 (3)	171 (3)
N(21)—H(21)···O(2^{i})	2.897 (2)	2.17 (2)	139 (2)
O(1)—H(1)···N(21^{i})	3.448 (2)	2.59 (3)	143 (2)
N(2)—H(2)···O(2^{ii})	2.934 (2)	2.28 (2)	129 (2)
N(2)—H(2)···O(21^{iii})	2.976 (2)	2.24 (3)	139 (2)
O(11)—H(11)···N(1^{iv})	2.703 (2)	1.67 (3)	176 (2)
O(11—H(11)···N(2^{iv})	3.433 (2)	2.49 (3)	151 (2)

Symmetry code: (i) $1 - x$, $1 - y$, $1 - z$; (ii) $x - \frac{1}{2}$, $\frac{1}{2} - y$, $z - \frac{1}{2}$; (iii) x, y, $z - 1$; (iv) x, y, $1 + z$.

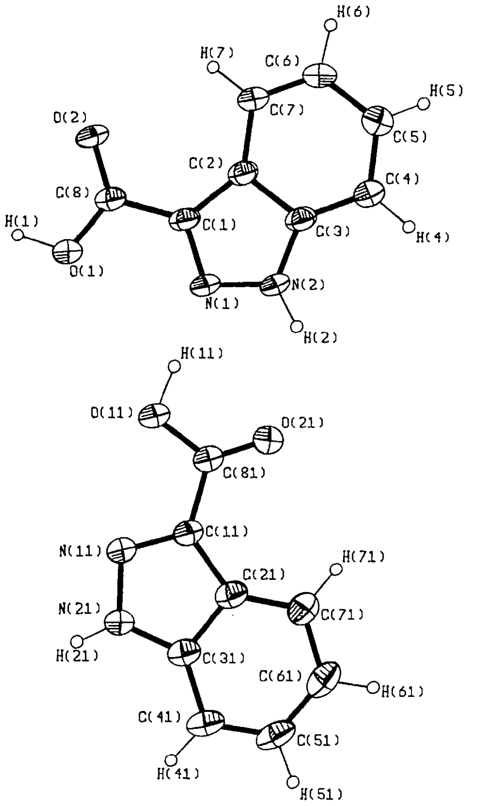

Fig. 1. Perspective view and atom labelling of the molecules. (Thermal ellipsoids are given at the 50% probability level.)

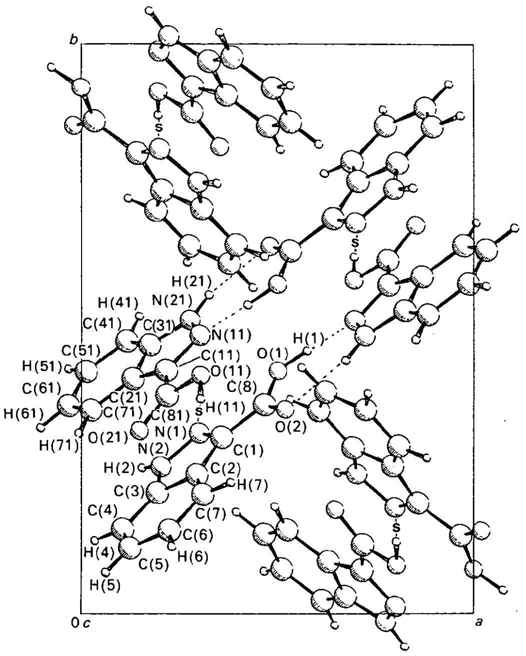

Fig. 2. Molecular packing viewed down the *c* axis. (The symbol s is for contacts at 1 + *z* or 1 − *z*.)

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