Indole-3-carboxylic acid

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Key indicators

Single-crystal X-ray study

T = 295 K

Mean $\sigma(\text{C}-\text{C}) = 0.003 \text{ \AA}$

R factor = 0.043

wR factor = 0.152

Data-to-parameter ratio = 14.6

For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

The crystal structure of indole-3-carboxylic acid, $\text{C}_9\text{H}_7\text{NO}_2$, shows the presence of centrosymmetric hydrogen-bonded cyclic carboxylic acid dimers [$\text{O} \cdots \text{O} = 2.649 (2) \text{ \AA}$]. These dimers are linked into a sheet structure through peripheral intermolecular hydrogen bonds between the carboxylic acid groups and the hetero-amine group of the *n*-glide-related indole ring [$\text{O} \cdots \text{N} = 3.013 (2) \text{ \AA}$].

Comment

On the basis of hydrogen-bonding concepts for carboxylic acids (Donohue, 1952), all strong proton-donor groups will form hydrogen bonds with suitable proton acceptors. Furthermore, if intramolecular hydrogen bonding is not possible, intermolecular $R_2^2(8)$ cyclic hydrogen-bonded dimer formation (Bernstein *et al.*, 1990; Etter, 1990) is the preferred interactive mode for simple carboxylic acids (Etter, 1991). This motif certainly has the highest incidence among monocarboxylic and dicarboxylic acids [95.5% probability (Allen *et al.*, 1998)], with occasional formation of the linear catemer motif (Leiserowitz, 1976), *e.g.* (2-formylphenoxy)acetic acid (Kennard *et al.*, 1985). However, with acids having additional interactive functional groups, the dimer units may be extended into ribbon or sheet structures through peripheral hydrogen-bonding interactions (Leiserowitz, 1976), or the dimer may be absent altogether, such as is found with the hydroxy acids, *e.g.* glycolic acid (Ellison *et al.*, 1971; Pijper, 1971). This variation is reflected in the 33% actual occurrence of the dimer motif among the 2541 carboxylic acid structures in the Cambridge Structural Database (CSD) (Allen *et al.*, 1998).

The title compound, indole-3-carboxylic acid, (I), is an example of an acid having a potentially interactive secondary group and was isolated as the major crystalline material from the attempted preparation of a proton-transfer compound of (I). Although the crystal structure of indole-3-acetic acid (IAA) is known (Karle *et al.*, 1964), the structure of (I) had not been previously reported, and therefore its structure was investigated and is reported here. This determination shows the presence of the usual primary hydrogen-bonded cyclic carboxylic acid dimers located across inversion centres in the unit cell (Figs. 1 and 2) [$\text{O31}-\text{H31} \cdots \text{O32}^i = 2.649 (2) \text{ \AA}$ and

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Figure 1

The molecular configuration and atom-naming scheme for (I), with non-H atoms shown as 40% probability displacement ellipsoids

O—H...O = 168 (2)°; symmetry code: (i) $2 - x, 1 - y, -z$. The carboxylic acid group is close to being coplanar with the indole ring [torsion angle C2—C3—C31—O32 = -168.5 (2)°].

The dimer units are extended laterally into a sheet structure through interactions between carboxylic acid O atoms and *n*-glide-related indole hetero-amine groups [$N1-H1...O32^{ii} = 3.013$ (2) Å and N—H...O = 164 (2)°; symmetry code: (ii) $\frac{1}{2} - x, \frac{1}{2} + y, -\frac{1}{2} - z$]. In this respect, the structure differs from that of indole-3-acetic acid (Karle *et al.*, 1964), where the dimers are not associated by formal hydrogen bonds involving the indole hetero-N atom.

Experimental

The title compound, (I), was isolated as large colourless flat prismatic crystals from the attempted preparation of a proton-transfer compound of indole-3-carboxylic acid with 8-hydroxyquinoline in an 80% ethanol/water solution, followed by slow evaporation. Literature m.p. 483–484 K (Mehta *et al.*, 1978) and 492–495 K (Bergman *et al.*, 1977).

Crystal data

$C_9H_7NO_2$	$D_x = 1.415 \text{ Mg m}^{-3}$
$M_r = 161.16$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/n$	Cell parameters from 25 reflections
$a = 16.048$ (3) Å	$\theta = 12.5\text{--}17.4^\circ$
$b = 10.611$ (3) Å	$\mu = 0.10 \text{ mm}^{-1}$
$c = 4.4588$ (16) Å	$T = 295$ (2) K
$\beta = 94.95$ (2)°	Block, colourless
$V = 756.5$ (4) Å ³	$0.40 \times 0.35 \times 0.15 \text{ mm}$
$Z = 4$	

Data collection

Rigaku AFC-7R diffractometer	$h = -20 \rightarrow 20$
ω -2 θ scans	$k = 0 \rightarrow 13$
2023 measured reflections	$l = -5 \rightarrow 2$
1723 independent reflections	3 standard reflections
1148 reflections with $I > 2\sigma(I)$	every 150 reflections
$R_{int} = 0.054$	intensity decay: 1.0%
$\theta_{max} = 27.5^\circ$	

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.1P)^2 + 0.2856P]$
$R[F^2 > 2\sigma(F^2)] = 0.043$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.152$	$(\Delta/\sigma)_{max} = 0.004$
$S = 0.93$	$\Delta\rho_{max} = 0.20 \text{ e \AA}^{-3}$
1723 reflections	$\Delta\rho_{min} = -0.26 \text{ e \AA}^{-3}$
118 parameters	
H atoms treated by a mixture of independent and constrained refinement

Figure 2

Perspective view of the packing in the unit cell, viewed down the *c* axis, showing the hydrogen-bonding associations as broken lines.

H atoms involved in hydrogen-bonding interactions (H1 and H31) were located by difference Fourier methods and their positional and isotropic displacement parameters were refined. Other H atoms were included at calculated positions (C—H = 0.96 Å) in the refinement as riding models [$U_{iso}(H) = 1.15U_{eq}(C)$].

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1999); cell refinement: *TEXSAN for Windows* (Molecular Structure Corporation, 1999); data reduction: *TEXSAN for Windows*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON for Windows* (Spek, 1999); software used to prepare material for publication: *PLATON for Windows*.

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