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Indole-3-carboxylic acid

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Key indicators

Single-crystal X-ray study
T = 295 K
Mean σ(C–C) = 0.003 Å
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.

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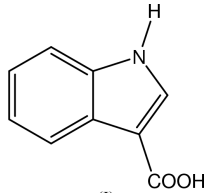
The crystal structure of indole-3-carboxylic acid, $C_9H_7NO_2$, shows the presence of centrosymmetric hydrogen-bonded cyclic carboxylic acid dimers [O···O = 2.649 (2) Å]. These dimers are linked into a sheet structure through peripheral intermolecular hydrogen bonds between the carboxylic acid groups and the hetero-amine group of the *n*-glide-related indole ring [O···N = 3.013 (2) Å].

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).



(I)

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) [O31—H31···O32^{i} = 2.649 (2) Å and

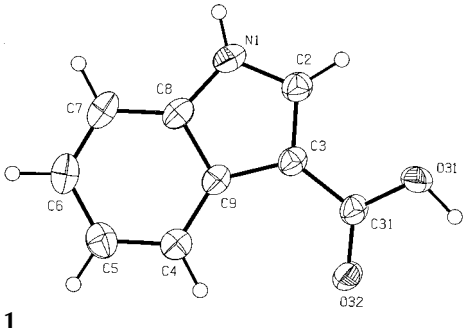


Figure 1
The molecular configuration and atom-naming scheme for (I), with non-H atoms shown as 40% probability displacement ellipsoids

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

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

Data collection

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

Refinement

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

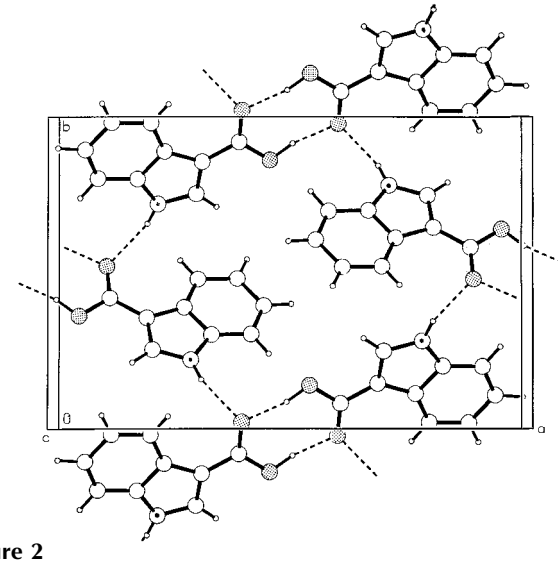


Figure 2
Perspective view of the packing in the unit cell, viewed down the *c* axis, showing the hydrogen-bonding associations as broken lines.

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: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *PLATON for Windows* (Spek, 1999); software used to prepare material for publication: *PLATON for Windows*.

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