

used to solve structure: *SHELXS86* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *ORTEX* (McArdle, 1993).

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, bond distances and angles involving non-H atoms, and torsion angles have been deposited with the IUCr (Reference: AS1213). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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## 2-Phenylquinoline-4-carboxylic Acid

ANTHONY C. BLACKBURN, ALLISON J. DOBSON AND  
ROGER E. GERKIN

Department of Chemistry, The Ohio State University,  
Columbus, Ohio 43210, USA. E-mail: rgerkin@magnus.acs.  
ohio-state.edu

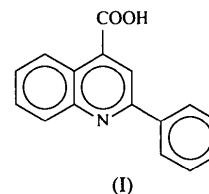
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### Abstract

In 2-phenylquinoline-4-carboxylic acid,  $C_{16}H_{11}NO_2$ , hydrogen bonding occurs only between a carboxy O-atom donor and the ring N atom, which acts as an acceptor. The carboxy H atom is ordered in this structure. The dihedral angle between the plane of the carboxy group and the best-fit mean quinoline plane is  $53.6(1)^\circ$ . All bond distances and angles within the quinoline core, the carboxy group and the phenyl group fall within the normal ranges. The structure is described in space group  $P2_12_12_1$

### Comment

As part of a continuing series of investigations of hydrogen bonding in organic solids, we describe here the structure of 2-phenylquinoline-4-carboxylic acid, (I), the structure of which has not been reported previously.



The title molecule is shown in Fig. 1 with the numbering system and a stereoview of the structure is presented in Fig. 2. Selected bond lengths and angles are compiled in Table 2 and these data support the assignment of hydrogen bonds for this structure in which atom O(1) is the sole donor and the N atom of the quinoline moiety is the sole acceptor. Consistent with this, the carboxy H-atom position is ordered in this structure.

Takusagawa, Hirotsu & Shimada (1973) presented graphically a smooth curvilinear correlation between the N—H<sub>carboxy</sub> distance and the C—N—C<sub>ring</sub> bond angle based upon their data for four pyridine dicarboxylic acids, namely, dipicolinic monohydrate, dinicotinic, cinchomeric and quinolinic. In these acids, the N—H<sub>carboxy</sub> distances ranged from 0.89(4) to 2.17(6) Å, while the C—N—C<sub>ring</sub> angles ranged from 116.8(4) to 125.3(2)°. Although corresponding data obtained subsequently for isonicotinic acid (pyridine-4-carboxylic acid) (Takusagawa & Shimada, 1976) conform well to that correlation, those for both nicotinic acid (pyridine-3-carboxylic acid) (Kutoglu & Scheringer, 1983) and the present compound do not. It thus appears that the degree of correlation shown initially was largely fortuitous.

All bond distances and angles within the quinoline core, the carboxy group and the phenyl group fall within the normal ranges. The mean deviation of the quinoline core atoms from the least-squares best-fit plane through them is 0.022(3) Å, the maximum deviation being 0.040(3) Å for atom C(7). For the phenyl group, the corresponding mean deviation is 0.004(3) Å, the maximum deviation being 0.006(3) Å for atom C(13). The dihedral angle between these two planes is 37.0(1)°. The dihedral angle between the best-fit quinoline plane and the carboxy group plane is 53.6(1)°.

Apart from the hydrogen bonding, four of the five closest approaches between molecules in this structure are between the carboxy H atom, H(1), of one molecule and atoms H(17), C(2), C(9) and C(17) of two other molecules; the fifth close approach occurs between atom O(1) and an H(17) atom. These five approach distances are all at least 0.12 Å less than the sums of the corresponding van der Waals radii.

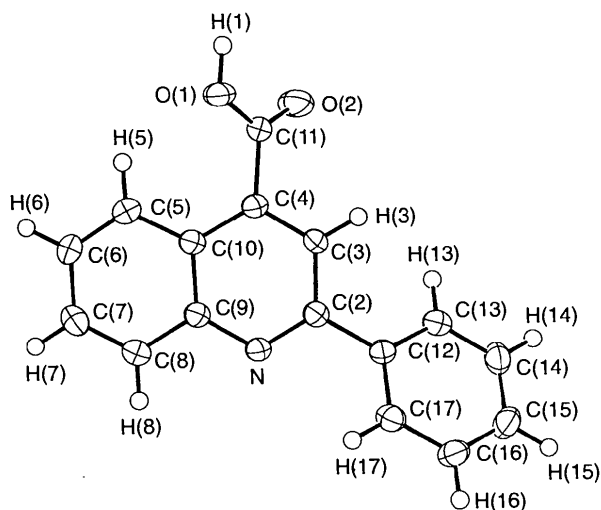


Fig. 1. An ORTEP drawing (Johnson, 1976) of 2-phenylquinoline-4-carboxylic acid showing the atomic numbering scheme. Displacement ellipsoids are drawn at 50% probability for all atoms except H for which they have been set artificially small.

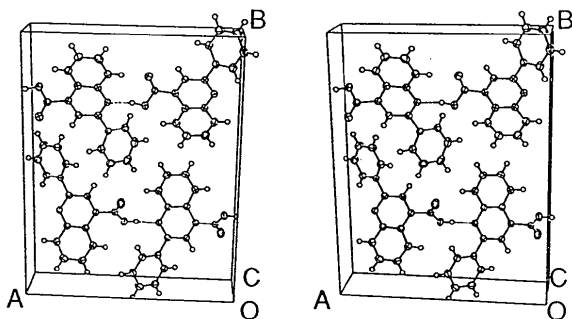


Fig. 2. A stereoview of a unit cell of the title structure (ORTEP II; Johnson, 1976) looking down a direction near the *c* axis. Displacement ellipsoids are drawn at 50% probability for all atoms except H for which they have been set artificially small.

## Experimental

2-Phenylquinoline-4-carboxylic acid (Aldrich) was dissolved in methanol, mixed with Norit-A decolorizing carbon and filtered. Since this compound has been described as being light sensitive, the filtrate was slowly evaporated in the dark at room temperature to produce clear colorless rods. A cut rod was mounted with epoxy cement on a glass fiber and analyzed with graphite-monochromated radiation.

### Crystal data

C<sub>16</sub>H<sub>11</sub>NO<sub>2</sub>

*M<sub>r</sub>* = 249.27

Orthorhombic

*P*2<sub>1</sub>2<sub>1</sub>2<sub>1</sub>

*a* = 15.379 (1) Å

*b* = 19.324 (1) Å

*c* = 3.915 (1) Å

Mo *K*α radiation

*λ* = 0.71073 Å

Cell parameters from 25 reflections

*θ* = 13.3–14.2°

*μ* = 0.088 mm<sup>-1</sup>

*T* = 296 K

*V* = 1163.4 (5) Å<sup>3</sup>

*Z* = 4

*D<sub>x</sub>* = 1.42 Mg m<sup>-3</sup>

*D<sub>m</sub>* not measured

Cut rod

0.35 × 0.11 × 0.11 mm

Colorless

### Data collection

Rigaku AFC-5S diffractometer

*ω*-2*θ* scans

Absorption correction:

none

2861 measured reflections

1639 independent reflections

1067 observed reflections

[*I* > 3σ(*I*)]

*R<sub>int</sub>* = 0.031

*θ*<sub>max</sub> = 27.56°

*h* = 0 → 20

*k* = 0 → 25

*l* = -5 → 5

6 standard reflections

monitored every 150

reflections

intensity variation: ±2.3%

(average maximum)

### Refinement

Refinement on *F*

*R* = 0.034

*wR* = 0.040

*S* = 1.42

1067 reflections

177 parameters

*w* = 1/σ<sup>2</sup>(*F*)

(Δ/σ)<sub>max</sub> < 0.01

Δρ<sub>max</sub> = 0.19 e Å<sup>-3</sup>

Δρ<sub>min</sub> = -0.17 e Å<sup>-3</sup>

Extinction correction:

Zachariasen (1963, 1968)

Extinction coefficient:

1.0 (3) × 10<sup>-6</sup>

Atomic scattering factors

from Cromer & Waber

(1974) for C, O and

N atoms, and Stewart,

Davidson & Simpson

(1965) for H atoms

Table 1. Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å<sup>2</sup>)

*U*<sub>iso</sub> for H(1); *U*<sub>eq</sub> = (1/3)Σ<sub>*i*</sub>Σ<sub>*j*</sub>*U*<sub>*ij*</sub>*a*<sub>*i*</sub><sup>\*</sup>*a*<sub>*j*</sub><sup>\*</sup> for all other atoms.

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> <sub>eq</sub> / <i>U</i> <sub>iso</sub>
O(1)	0.0511 (1)	0.2754 (1)	-0.0776 (7)	0.0387 (6)
O(2)	0.0622 (1)	0.1787 (1)	0.2294 (7)	0.0517 (7)
N	0.3747 (1)	0.2299 (1)	0.0185 (6)	0.0292 (6)
C(2)	0.3286 (2)	0.1748 (1)	-0.0719 (8)	0.0283 (7)
C(3)	0.2365 (2)	0.1746 (1)	-0.0555 (8)	0.0297 (7)
C(4)	0.1923 (2)	0.2322 (1)	0.0462 (8)	0.0296 (7)
C(5)	0.2002 (2)	0.3542 (2)	0.2569 (9)	0.0382 (8)
C(6)	0.2500 (2)	0.4085 (1)	0.3609 (10)	0.0417 (9)
C(7)	0.3412 (2)	0.4039 (2)	0.3556 (9)	0.0432 (9)
C(8)	0.3812 (2)	0.3454 (2)	0.2423 (9)	0.0377 (8)
C(9)	0.3317 (2)	0.2881 (1)	0.1289 (8)	0.0285 (7)
C(10)	0.2393 (2)	0.2924 (1)	0.1407 (8)	0.0281 (7)
C(11)	0.0945 (2)	0.2260 (2)	0.0763 (8)	0.0309 (7)
C(12)	0.3753 (2)	0.1112 (1)	-0.1814 (7)	0.0288 (7)
C(13)	0.3431 (2)	0.0464 (1)	-0.0913 (9)	0.0344 (7)
C(14)	0.3879 (2)	-0.0130 (1)	-0.1803 (8)	0.0393 (9)
C(15)	0.4645 (2)	-0.0090 (2)	-0.3614 (9)	0.0439 (9)
C(16)	0.4962 (2)	0.0551 (2)	-0.4565 (9)	0.0404 (8)
C(17)	0.4523 (2)	0.1150 (1)	-0.3675 (8)	0.0324 (8)
H(1)	-0.009 (3)	0.269 (2)	-0.023 (13)	0.09 (1)

Table 2. Selected geometric parameters (Å, °)

N—C(2)	1.328 (3)	C(2)—C(12)	1.486 (3)
N—C(9)	1.374 (3)	C(12)—C(13)	1.392 (4)
C(2)—C(3)	1.418 (3)	C(13)—C(14)	1.383 (4)
C(3)—C(4)	1.364 (4)	C(14)—C(15)	1.377 (4)
C(4)—C(10)	1.419 (4)	C(15)—C(16)	1.381 (4)
C(5)—C(6)	1.362 (4)	C(16)—C(17)	1.385 (4)
C(5)—C(10)	1.411 (4)	C(17)—C(12)	1.392 (4)
C(6)—C(7)	1.406 (4)	C(4)—C(11)	1.513 (3)
C(7)—C(8)	1.361 (4)	C(11)—O(1)	1.312 (3)
C(8)—C(9)	1.416 (4)	C(11)—O(2)	1.200 (3)
C(9)—C(10)	1.425 (3)		

C(2)—N—C(9)	118.9 (2)	C(4)—C(10)—C(5)	124.1 (2)
N—C(2)—C(3)	121.5 (2)	C(4)—C(10)—C(9)	116.8 (2)
N—C(2)—C(12)	118.8 (2)	C(5)—C(10)—C(9)	119.0 (2)
C(3)—C(2)—C(12)	119.7 (2)	C(2)—C(12)—C(17)	121.3 (2)
C(2)—C(3)—C(4)	120.6 (2)	C(12)—C(13)—C(14)	120.3 (2)
C(3)—C(4)—C(10)	119.5 (2)	C(13)—C(14)—C(15)	120.6 (3)
C(3)—C(4)—C(11)	116.9 (2)	C(14)—C(15)—C(16)	119.4 (3)
C(10)—C(4)—C(11)	123.5 (2)	C(15)—C(16)—C(17)	120.6 (3)
C(6)—C(5)—C(10)	120.5 (2)	C(16)—C(17)—C(12)	120.2 (3)
C(5)—C(6)—C(7)	120.6 (3)	C(17)—C(12)—C(13)	118.8 (2)
C(6)—C(7)—C(8)	120.5 (3)	O(1)—C(11)—O(2)	125.0 (2)
C(7)—C(8)—C(9)	120.6 (2)	O(1)—C(11)—C(4)	114.3 (2)
N—C(9)—C(8)	118.7 (2)	O(2)—C(11)—C(4)	120.7 (3)
N—C(9)—C(10)	122.6 (2)	C(11)—O(1)—H(1)	107 (2)
C(8)—C(9)—C(10)	118.7 (2)		

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
O(1)—H(1) $\cdots$ N <sup>i</sup>	0.96 (4)	1.79 (4)	2.725 (3)	165 (4)

Symmetry code: (i)  $x - \frac{1}{2}, \frac{1}{2} - y, -z$ .

The scan widths used were  $(1.20 + 0.35 \tan \theta)^\circ$  in  $\omega$ , with a background/scan time ratio of 0.5. No correction was required for decay or absorption but the data were corrected for Lorentz and polarization effects. The Laue symmetry and systematic absences allowed unique determination of the space group as  $P2_12_12_1$ ; refinement proceeded well and it was adopted. The direct-methods program *DIREX* (Parthasarathi, Beurskens & Slot, 1983) produced an *E* map from which the initial positions of the C, N and O atoms were identified. Difference Fourier methods were used to locate the initial H-atom positions. Full-matrix least-squares refinement was performed using *TEXSAN* (Molecular Structure Corporation, 1989). In the later stages of refinement, ring H atoms were assigned fixed geometry (C—H 0.96 Å) and isotropic displacement parameters of magnitude 1.2 times those of the attached C atoms. The carboxy H atom was refined isotropically. Also in the late stages, a secondary extinction parameter (Zachariasen, 1963, 1968) was included; the maximum effect of extinction was 2.9% of  $F_o$  for 011. The maximum peak on the final difference map was located at (0.21, 0.26, 0.08), near the midpoint of the C(4)—C(10) bond; the minimum peak was located at (0.28, 0.23, 1.020), approximately equidistant from atoms C(2), C(3) and N.

Data collection: *MSC/AFCDiffractometer Control Software* (Molecular Structure Corporation, 1988). Cell refinement: *MSC/AFCDiffractometer Control Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1989). Molecular graphics: *ORTEPII* (Johnson, 1976). Software used to prepare material for publication: *TEXSAN*.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, complete geometry and least-squares-planes data have been deposited with the IUCr (Reference: BK1182). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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## Unsymmetrically Substituted Thioureas. 1,1-Dimethyl-3-*o*-tolylthiourea and 1,1-Diethyl-3-*o*-tolylthiourea

AKILAN RAMNATHAN,<sup>a</sup> KANDASAMY SIVAKUMAR,<sup>a</sup>  
 NARAYANASAMY JANARTHANAN,<sup>b</sup> DRAVIDA MEERARANI,<sup>b</sup>  
 KRISHNAMOORTHY RAMADAS<sup>b</sup> AND HOONG-KUN FUN<sup>c</sup>

<sup>a</sup>Department of Physics, Anna University, Madras 600 025, India, <sup>b</sup>Centre for Agrochemical Research, SPIC Science Foundation, 110 Mount Road, Madras 600 032, India, and <sup>c</sup>X-Ray Crystallography Unit, School of Physics, Universiti Sains Malaysia, 11800 USM, Penang, Malaysia

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## Abstract

The two unsymmetrically substituted thiourea derivatives, 1,1-dimethyl-3-*o*-tolylthiourea, C<sub>10</sub>H<sub>14</sub>N<sub>2</sub>S, and 1,1-diethyl-3-*o*-tolylthiourea, C<sub>12</sub>H<sub>18</sub>N<sub>2</sub>S, both crystallize in the orthorhombic space group  $P2_12_12_1$  and have the same type of crystal packing. In both structures, N—H  $\cdots$  S hydrogen bonds link the molecules into chains along the *b* axis.

## Comment

Crystal structure analyses of the title compounds form part of our studies of substituted thiourea derivatives. Unsymmetrically substituted thioureas exhibit agrochemical properties (Sarkis & Faisal, 1985). Our interest is focused on the molecular conformations and N—H  $\cdots$  S hydrogen bonding in substituted thiourea derivatives in the solid state. The structure determinations of the title compounds, 1,1-dimethyl-3-*o*-tolylthiourea

† Visiting Post Doctoral Research Fellow at the School of Physics, Universiti Sains Malaysia, 11800 USM, Penang, Malaysia.