Table 4. *Selected geometric parameters (Å, °) for the butyl compound*

O1*A*—C21*A*	1.335 (4)	O1*B*—C21*B*	1.329 (5)
O1*A*—C22*A*	1.444 (4)	O1*B*—C22*B*	1.431 (5)
O2*A*—C21*A*	1.205 (4)	O2*B*—C21*B*	1.198 (4)
O3*A*—C14*A*	1.365 (4)	O3*B*—C14*B*	1.361 (3)
O3*A*—C11*A*	1.383 (2)	O3*B*—C11*B*	1.383 (2)
O4*A*—C14*A*	1.204 (3)	O4*B*—C14*B*	1.200 (3)
O5*A*—C18*A*	1.367 (3)	O5*B*—C18*B*	1.356 (3)
O5*A*—C31*A*	1.434 (4)	O5*B*—C31*B*	1.432 (4)
N1*A*—C7*A*	1.261 (4)	N1*B*—C7*B*	1.275 (4)
N1*A*—C4*A*	1.423 (3)	N1*B*—C4*B*	1.419 (3)
C1*A*—C21*A*	1.478 (4)	C1*B*—C21*B*	1.469 (4)
C8*A*—C7*A*	1.463 (4)	C8*B*—C7*B*	1.451 (3)
C15*A*—C14*A*	1.463 (3)	C15*B*—C14*B*	1.464 (3)
C7*A*—N1*A*—C4*A*	118.8 (2)	C7*B*—N1*B*—C4*B*	117.3 (3)
N1*A*—C7*A*—C8*A*	123.5 (3)	N1*B*—C7*B*—C8*B*	123.8 (3)

For the ethyl compound ($n = 2$), all the non-H atoms were refined anisotropically. For the butyl compound ($n = 4$), the C25 atoms had remarkably large displacement parameters and considerably high peaks were found around them. Thus, these atoms were disordered in further refinements. Occupancies were fixed at 0.4 for atoms C25*A* and C25*B* and 0.3 for atoms C25*A*′, C25*A*″, C25*B*′ and C25*B*″. All the non-H atoms were refined anisotropically, except for C24*B* and the disordered C25 atoms. The butyl chains were refined with distance constraints due to the disordering. All the benzene rings were constrained to have regular hexagonal geometry, with C—C distances of 1.39 Å. The H atoms attached to atom C7 of the azomethine groups were found in the difference Fourier maps and refined isotropically, while all other H atoms (except for those attached to the C24 and C25 atoms of the butyl compound) were calculated geometrically (C—H distances were constrained to be 0.96 Å for primary H atoms, 0.97 Å for secondary and 0.93 Å for aromatic) and not refined.

For both compounds, data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1992*a*); cell refinement: *MSC/AFC Diffractometer Control Software*; data reduction: *TEXSAN* (Molecular Structure Corporation, 1992*b*). Program(s) used to solve structures: *MULTAN*88 (Debaerdemaeker, Tate & Woolfson, 1985) for the ethyl compound; *MITHRIL*90 (Gilmore, 1984) for the butyl compound. For both compounds, program(s) used to refine structures: *SHELXL*93 (Sheldrick, 1993); molecular graphics: *TEXSAN*; software used to prepare material for publication: *SHELXL*93 (Sheldrick, 1993).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: AS1215). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Debaerdemaeker, T., Tate, C. & Woolfson, M. M. (1985). *Acta Cryst.* A**41**, 286–290.

Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.

Gilmore, G. J. (1984). *J. Appl. Cryst.* **17**, 42–46.

Lotke, S. & Patil, R. N. (1989). *Mol. Cryst. Liq. Cryst.* **166**, 43–60.

Molecular Structure Corporation (1992*a*). *MSC/AFC Diffractometer Control Software*. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.

Molecular Structure Corporation (1992*b*). *TEXSAN. TEXRAY Structure Analysis Package*. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.

Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.

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Xanthurenic Acid Monohydrate

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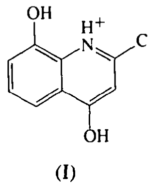
Abstract

In the structure of the title compound, 4,8-dihydroxy-2-quinolinecarboxylic acid monohydrate, $C_{10}H_7NO_4.H_2O$, the ionized carboxy group is located in the quinoline ring plane and the N atom of the ring is protonated so that it is positively charged, *i.e.* the compound may be named 4,8-dihydroxyquinolinium-2-carboxylate monohydrate. The crystal structure is stabilized by intermolecular O—H···O hydrogen bonds involving the water molecule.

Comment

Xanthurenic acid, (I), is a well known tryptophan metabolite which is induced from kynurenin as a result of vitamin B_6 deficiency. This metabolite occurs in the urine of humans, monkeys and rats when dietry vitamin B_6 is inadequate (Martin, Mayes & Rodwell, 1983). Xanthurenic acid has been reported to form a complex with insulin and damage pancreatic β cells (Kotake *et al.*, 1968; Murakami, 1968). Also, an increase in its formation may alter glucose metabolism (Seifert & Pewnim, 1992).



(I)

In order to elucidate the metabolic pathway of tryptophan metabolites, accurate structural and conformational information is indispensable. We have thus undertaken the structural analysis of the title compound.

The molecular structure is shown in Fig. 1, with the unit-cell packing in Fig. 2. The carboxy group is ionized and coplanar with the quinoline ring. The N atom of the ring is protonated. An intramolecular hydrogen bond is formed between the protonated N(1) atom and the O(1) atom [N(1)—H(1)···O(1) 2.625 (4) Å]. In the crystal structure, the molecules are connected by hydrogen bonds involving the water molecule: O(4)—H(4)···O(3^{i}) 2.789 (4), O(8)—H(8)···O(3^{ii}) 3.131 (4), O(3)···O(2^{iii}) 2.829 (4) and O(3)···O(2^{iv}) 2.837 (4) Å [symmetry codes: (i) $x, \frac{1}{2}-y, -\frac{1}{2}+z$; (ii) $x, \frac{1}{2}-y, -\frac{3}{2}+z$; (iii) $-x, 1-y, 1-z$; (iv) $x, -1+y, 1+z$]. There is no significant ring stacking.

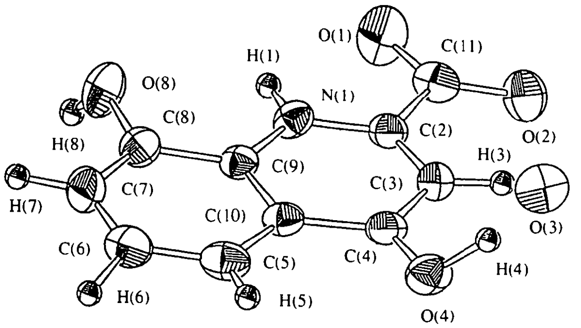


Fig. 1. An *ORTEP*II drawing (Johnson, 1976) of the title compound with the atomic numbering scheme. Ellipsoids for non-H atoms correspond to 50% probability.

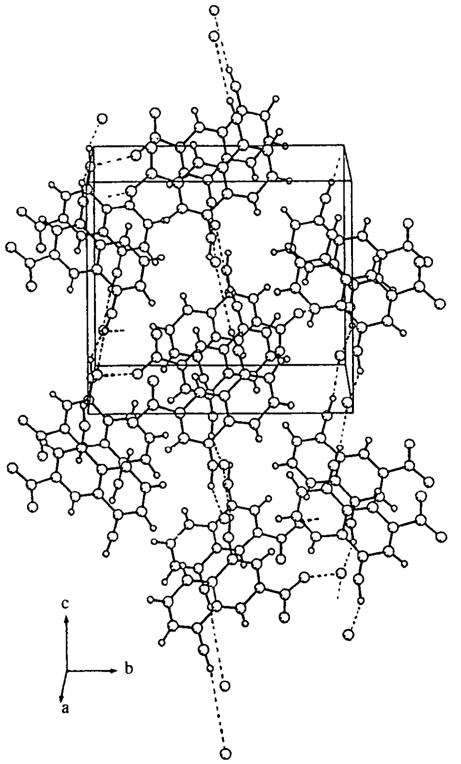


Fig. 2. A packing diagram of the title compound viewed along the *a* axis of the unit cell; intermolecular hydrogen bonds are represented by dashed lines.

Experimental

A single light-brown prismatic crystal was obtained by the slow evaporation of an approximately 95% methanol solution of xanthurenic acid at room temperature, the pH of the solution being adjusted to neutral with dilute aqueous ammonia solution.

Crystal data

$C_{10}H_7NO_4.H_2O$
$M_r = 223.18$
Monoclinic
$P2_1/c$
$a = 7.710(5)$ Å
$b = 12.354(2)$ Å
$c = 10.920(2)$ Å
$\beta = 106.92(2)°$
$V = 995.1(7)$ Å^3
$Z = 4$
$D_x = 1.490$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 25 reflections
$\theta = 15.45–19.35°$
$\mu = 0.114$ mm^{-1}
$T = 296$ K
Prism
0.4 × 0.1 × 0.1 mm
Light brown

Data collection

Rigaku AFC-5*R* diffractometer
ω–2θ scans
Absorption correction: none
2565 measured reflections
2397 independent reflections
1473 observed reflections [$I > 2\sigma(I)$]

$R_{\rm int} = 0.031$
$\theta_{\rm max} = 27.50°$
$h = 0 \rightarrow 10$
$k = 0 \rightarrow 15$
$l = -13 \rightarrow 13$
3 standard reflections monitored every 150 reflections intensity decay: 0.3%

Refinement

Refinement on F
$R = 0.072$
$wR = 0.087$
$S = 2.64$
1473 reflections
145 parameters
H atom parameters not refined
$w = 4F_o^2/\sigma^2(F_o^2)$

$(\Delta/\sigma)_{\rm max} = 0.018$
$\Delta\rho_{\rm max} = 0.52$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.42$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$$B_{\rm eq} = (8\pi^2/3)\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$B_{\rm eq}$
O(1)	−0.0327 (4)	0.7532 (3)	−0.1460 (3)	4.4 (1)
O(2)	0.0415 (4)	0.8318 (2)	0.0473 (3)	3.7 (1)
O(3)	0.2427 (4)	0.0145 (3)	1.0093 (3)	4.7 (2)
O(4)	0.4092 (3)	0.5304 (2)	0.3200 (2)	3.2 (1)
O(8)	0.1496 (4)	0.4297 (2)	−0.2373 (2)	3.5 (1)
N(1)	0.1521 (4)	0.5774 (3)	−0.0566 (3)	2.3 (1)
C(2)	0.1454 (4)	0.6538 (3)	0.0287 (3)	2.3 (1)
C(3)	0.2292 (5)	0.6401 (3)	0.1554 (4)	2.6 (1)
C(4)	0.3316 (5)	0.5454 (3)	0.2026 (3)	2.4 (1)
C(5)	0.4403 (5)	0.3685 (3)	0.1409 (4)	3.0 (2)
C(6)	0.4396 (5)	0.2930 (3)	0.0488 (4)	3.3 (2)
C(7)	0.3427 (6)	0.3109 (3)	−0.0787 (4)	3.4 (2)
C(8)	0.2463 (5)	0.4056 (3)	−0.1154 (4)	2.6 (2)
C(9)	0.2480 (5)	0.4834 (3)	−0.0212 (3)	2.2 (1)
C(10)	0.3432 (5)	0.4662 (3)	0.1079 (3)	2.3 (1)
C(11)	0.0415 (5)	0.7550 (3)	−0.0279 (4)	2.9 (2)

Table 2. *Selected geometric parameters (Å, °)*

O(1)—C(11)	1.250 (5)	C(3)—C(4)	1.421 (5)
O(2)—C(11)	1.254 (5)	C(4)—C(10)	1.446 (5)
O(4)—C(4)	1.261 (4)	C(5)—C(6)	1.370 (6)
O(8)—C(8)	1.356 (5)	C(5)—C(10)	1.410 (5)
N(1)—C(2)	1.337 (5)	C(6)—C(7)	1.393 (6)
N(1)—C(9)	1.370 (4)	C(7)—C(8)	1.382 (6)
C(2)—C(3)	1.356 (5)	C(8)—C(9)	1.405 (5)
C(2)—C(11)	1.517 (5)	C(9)—C(10)	1.403 (5)
C(2)—N(1)—C(9)	121.9 (3)	O(8)—C(8)—C(9)	117.0 (3)
N(1)—C(2)—C(3)	121.3 (3)	C(7)—C(8)—C(9)	118.5 (4)
N(1)—C(2)—C(11)	114.9 (3)	N(1)—C(9)—C(8)	119.0 (3)
C(3)—C(2)—C(11)	123.8 (3)	N(1)—C(9)—C(10)	119.6 (3)
C(2)—C(3)—C(4)	121.5 (3)	C(8)—C(9)—C(10)	121.5 (3)
O(4)—C(4)—C(3)	122.6 (4)	C(4)—C(10)—C(5)	122.4 (3)
O(4)—C(4)—C(10)	121.2 (3)	C(4)—C(10)—C(9)	119.5 (3)
C(3)—C(4)—C(10)	116.2 (3)	C(5)—C(10)—C(9)	118.0 (3)
C(6)—C(5)—C(10)	120.4 (4)	O(1)—C(11)—O(2)	127.0 (4)
C(5)—C(6)—C(7)	120.8 (4)	O(1)—C(11)—C(2)	115.7 (4)
C(6)—C(7)—C(8)	120.7 (4)	O(2)—C(11)—C(2)	117.2 (3)
O(8)—C(8)—C(7)	124.5 (4)		

The H atoms bonded to the water O atom could not be located on a difference Fourier map. The relatively large R value of 0.072 may be a result of the crystal being extremely thin.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1985). Program(s) used to solve structure: *SHELX*86 (Sheldrick, 1985) and *DIRDIF* (Beurskens, 1984). Program(s) used to refine structure: *TEXSAN*. Molecular graphics: *ORTEP*II (Johnson, 1976).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: AS1218). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Beurskens, P. T. (1984). *DIRDIF. Direct Methods for Difference Structures – an Automatic Procedure for Phase Extension and Refinement of Difference Structure Factors*. Technical Report 1984/1. Crystallography Laboratory, Toernooiveld, 6525 ED Nijmegen, The Netherlands.

Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.

Kotake, Y., Sotokawa, T., Murakami, E., Hisatake, A., Abe, M. & Ikeda, Y. (1968). *J. Biochem.* **63**, 578–581.

Martin, D. W., Mayes, P. A. & Rodwell, V. W. (1983). *Harper's Review of Biochemistry*, pp. 464–479. Tokyo: Maruzen Asia.

Molecular Structure Corporation (1985). *TEXSAN. TEXRAY Structure Analysis Package*. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.

Molecular Structure Corporation (1988). *MSC/AFC Diffractometer Control Software*. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.

Murakami, E. (1968). *J. Biochem.* **63**, 573–577.

Seifert, J. & Pewnim, T. (1992). *Biochem. Pharmacol.* **44**, 2243–2250.

Sheldrick, G. M. (1985). *SHELXS86. Crystallographic Computing* 3, edited by G. M. Sheldrick, C. Krüger & R. Goddard, pp. 175–189. Oxford University Press.

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3,4-Diphenylpyrrole-2,5-dicarboxylic Acid Acetic Acid Disolvate

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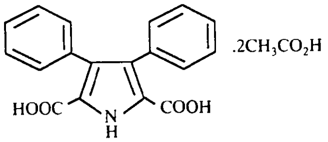
Abstract

3,4-Diphenylpyrrole-2,5-dicarboxylic acid crystallizes as the acetic acid disolvate, $C_{18}H_{13}NO_4.2CH_3CO_2H$, and exhibits extensive hydrogen bonding involving the carboxylic acid functional groups, the amine group and the acetic acid moieties. The phenyl rings were found to lie at an angle of nearly 50° with respect to the planar pyrrole ring.

Comment

As part of our investigations of substituted porphyrins, the title compound, (I) (Friedman, 1965), was synthesized.



(I)

Analysis of the structural information shows the phenyl rings (Fig. 1) to have torsion angles C(1)—C(2)—C(7)—C(8) and C(4)—C(3)—C(13)—C(18) of 52.8 (9) and 57.0 (8)°, respectively, with respect to the the planar pyrrole ring, rather than being perpendicular to it (Medforth, Senge, Smith, Sparks & Shelnut, 1992).

The carboxylic acid functionality of the substituted pyrrole ring and the acetic acid solvate molecules participate in extensive hydrogen bonding (Fig. 2). The hydrogen-bonding distances between the pyrrole dicarboxylic acid groups and the acetic acid molecules are O(3$^{\rm i}$)···H—O(8) 2.626 (6), O(4)—H···O(7$^{\rm i}$) 2.837 (6) [symmetry code: (i) $1-x$, $2-y$, $1-z$] and O(2)—H···O(5) 2.630 (6) Å, while the O(6)—H···O(7) distance between the acetic acid molecules is 2.686 (7) Å. Hydrogen bonding between the amine H atom and carboxy O atom of an adjacent pyrrole molecule [N(1)—H···O(1$^{\rm i}$) 2.969 (7) Å] results in a dimer-like structure having a center of symmetry between the N(1) and N(1$^{\rm i}$) atoms. The O—H···O and N—H···O hydro-

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