Acta Crystallographica Section C
Crystal Structure Communications
ISSN 0108-2701

2,6-Diphenylpyridine-4-carboxylic acid

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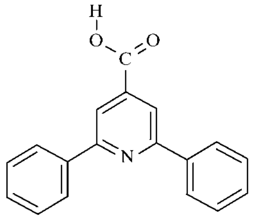
Received 15 October 2001
Accepted 18 October 2001
Online 22 December 2001

The distinctive feature of the crystal structure of 2,6-diphenylpyridine-4-carboxylic acid, $C_{18}H_{13}NO_2$, is the formation of intermolecular O—H···O hydrogen bonds that lead to the formation of centrosymmetric cyclic dimers with $R_2^2(8)$ topology. Molecules related by translation along the *b* axis exhibit strong π–π stacking of aromatic rings, with an average interplanar distance of 3.3 Å.

Comment

The most common packing motif of carboxylic acids is based on the formation of cyclic dimers through a pair of O—H···O bonds (Leiserowitz, 1976). By contrast, the solid-state chemistry of pyridinecarboxylic acids is dominated by the formation of an intermolecular O—H···N hydrogen bond between the carboxylic acid group and the pyridine N atom of a second molecule (Takusagawa & Shimada, 1976; Wright & King, 1953). The latter hydrogen-bonding interaction can be described more accurately as occurring *via* O—H···N or $^+$N—H···O$^-$, bonds depending on the tautomeric form present. Similar arguments also apply to other heterocyclic aromatic carboxylic acids, such as pyrazinic acid (Takusagawa *et al.*, 1974) and quinoline-4-carboxylic acid (Dobson & Gerkin, 1998). The directional nature of the O—H···N bonding interaction for the isonicotinic acid has been exploited in the promotion of highly oriented structures (O'Shea *et al.*, 2001). On the other hand, when carboxylic acid groups occupy both α and α' positions of the pyridine ring, as in dipicolinic acid, the N atom is not involved in head-to-tail interactions of the type described, although O—H···N hydrogen bonds with a cocrystallized water molecule are still present (Takusagawa *et al.*, 1973).



(I)

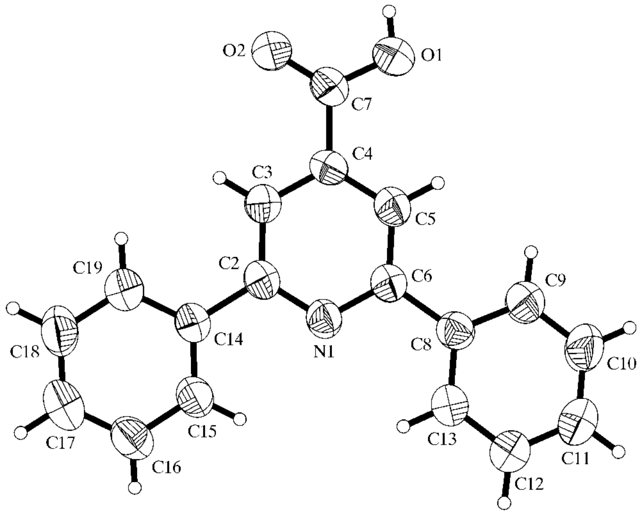


Figure 1
The molecular structure of (I) showing the atom-labelling scheme and displacement ellipsoids at the 50% probability level.

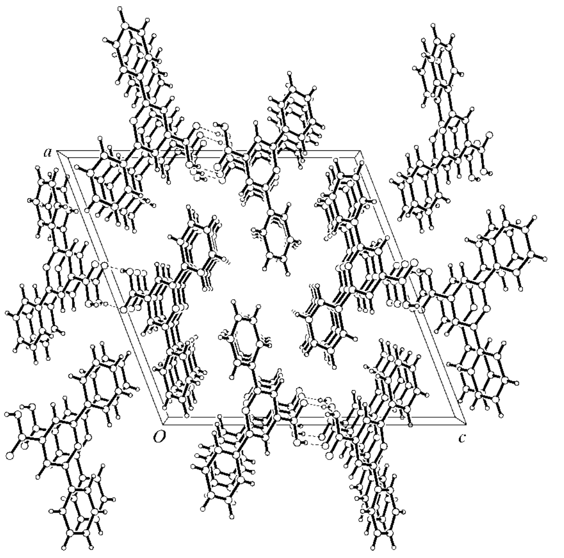


Figure 2
The crystal packing of (I) viewed down the *b* axis.

The molecular structure of (I) is shown in Fig. 1. Geometric parameters are normal (Table 1) and compare well with those of other 2,6-diphenylpyridines (Krygowski *et al.*, 1994; Silva *et al.*, 1997). The whole molecule is nearly planar, as clearly shown by the values of the torsion angles reported in Table 1. Dihedral angles between the best-fit plane of the pyridine and those of the phenyl substituents are 8.7 (1) (ring atoms C8–C13) and 9.8 (1)° (ring atoms C14–C19).

The supramolecular structure of (I) can be described in terms of π–π interactions and intermolecular hydrogen bonding (Table 2). In the crystal packing, the molecules are stacked along the *b* axis (Fig. 2). The shortest interplanar distance of 2.919 (2) Å is found between the C14–C19 phenyl

DOI: 10.1107/S0108270101017693

ring and its translation-related ring. The stacks are organized in a pseudo-herring-bone fashion since the $\pi\cdots$H interactions do not seem to be dominant like in a classical herring-bone stacking mode (Gavezzotti & Desiraju, 1988; André *et al.*, 1997). The dominant supramolecular interaction is the O—H$\cdots$O hydrogen bonding between centrosymmetric carboxylic acid groups (Fig. 3). The corresponding graph-set is therefore $R_2^2(8)$ (Etter *et al.*, 1990), which is typical for carboxyl dimers. In addition, a second motif with graph-set $R_6^4(44)$ can be identified in the crystal packing when weaker hydrogen bonds of the C—H$\cdots$O type are considered (Fig. 3).

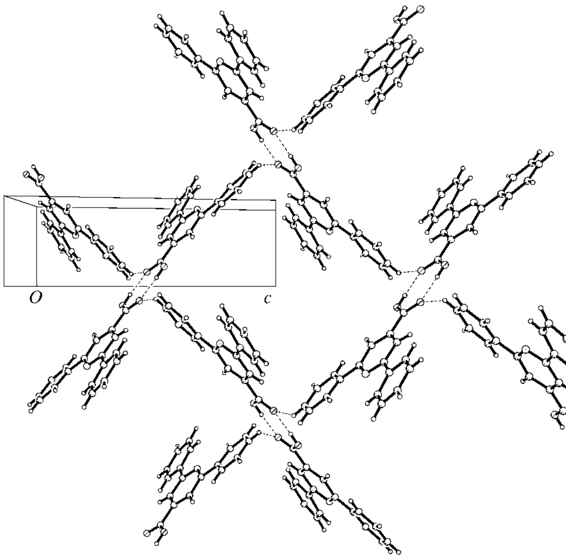


Figure 3
A partial view of the crystal structure of (I) showing the formation of ring motifs with graph-set $R_2^2(8)$ that further interact through lateral C—H$\cdots$O interactions to afford larger rings with graph-set $R_6^4(44)$.

Experimental

The title compound was prepared in one step from 3-benzoylacrylic acid and *N*-phenacylpyridinium bromide in the presence of excess ammonium acetate (Blumbergs *et al.*, 1972). The compound was recrystallized from hot acetic acid as pale-yellow crystals.

Crystal data

$C_{18}H_{13}NO_2$
$M_r = 275.29$
Monoclinic, $P2_1/n$
$a = 16.524$ (4) Å
$b = 5.2898$ (9) Å
$c = 17.021$ (3) Å
$\beta = 111.229$ (17)°
$V = 1386.8$ (5) Å^3
$Z = 4$

$D_x = 1.32$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 8.0$–$12.9°$
$\mu = 0.09$ mm^{-1}
$T = 293$ (2) K
Block, pale yellow
$0.23 \times 0.20 \times 0.17$ mm

Data collection

Siemens *R*3*m*/*V* diffractometer
$\theta/2\theta$ scans
2559 measured reflections
2469 independent reflections
980 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.069$
$\theta_{\rm max} = 25.1°$

$h = 0 \rightarrow 19$
$k = 0 \rightarrow 6$
$l = -20 \rightarrow 18$
2 standard reflections
frequency: 48 min
intensity decay: none

Table 1
Selected geometric parameters (Å, °).

N1—C2	1.343 (3)	C3—C4	1.378 (3)
N1—C6	1.350 (3)	C4—C5	1.365 (3)
O1—C7	1.297 (3)	C4—C7	1.478 (3)
O2—C7	1.243 (3)	C5—C6	1.394 (3)
C2—C3	1.393 (3)		
O2—C7—O1	122.8 (3)	O1—C7—C4	115.6 (3)
O2—C7—C4	121.6 (2)		
C3—C4—C7—O2	0.7 (4)	N1—C6—C8—C13	−7.6 (4)
C5—C4—C7—O1	4.1 (4)	N1—C2—C14—C15	−8.6 (3)

Table 2
Hydrogen-bonding geometry (Å, °).

D—H$\cdots$*A*	*D*—H	H$\cdots$*A*	*D*$\cdots$*A*	*D*—H$\cdots$*A*
O1—H1$\cdots$O2$^{\rm i}$	0.82	1.83	2.640 (3)	172
C11—H11$\cdots$O2$^{\rm ii}$	0.93	2.70	3.406 (3)	134

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

Refinement

Refinement on F^2
$R(F) = 0.045$
$wR(F^2) = 0.089$
$S = 0.87$
2469 reflections
190 parameters

H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0250P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max} = 0.13$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.13$ e Å^{-3}

Data collection: *XPREP* (Bruker, 1997); cell refinement: *XPREP*; data reduction: *XPREP*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *XP* (Bruker, 1997).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: NA1541). Services for accessing these data are described at the back of the journal.

References

André, I., Foces-Foces, C., Cano, F. H. & Martinez-Ripoll, M. (1997). *Acta Cryst.* B**53**, 996–1005.
Blumbergs, P., LaMontagne, M. P., Markovac, A., Moehring, J. G., Ash, A. B. & Stevens, C. L. (1972). *J. Med. Chem.* **15**, 808–812.
Bruker (1997). *XPREP* and *XP*. Bruker AXS Inc., Madison, Wisconsin, USA.
Dobson, A. J. & Gerkin, R. E. (1998). *Acta Cryst.* C**54**, 1883–1885.
Etter, M. C., MacDonald, J. C. & Bernstein, J. (1990). *Acta Cryst.* B**46**, 256–262.
Gavezzotti, A. & Desiraju, G. R. (1988). *Acta Cryst.* B**44**, 427–434.
Krygowski, T. M., Anulewicz, R., Jarmula, A., Bak, T., Rasala, D. & Howard, S. (1994). *Tetrahedron*, **50**, 13155–13164.
Leiserowitz, L. (1976). *Acta Cryst.* B**32**, 775–802.
O'Shea, J. N., Schnadt, J., Brühwiler, P. A., Hillesheimer, H., Mårtensson, N., Patthey, L., Krempasky, J., Wang, C.-K. & Ågren, H. (2001). *J. Phys. Chem.* **105**, 1917–1920.
Sheldrick, G. M. (1997). *SHELXS*97 and *SHELXL*97. University of Göttingen, Germany.
Silva, A. M. S., Almeida, L. M. P. M., Cavaleiro, J. A. S., Foces-Foces, C., Llamas-Saiz, A. L., Fontenas, C., Jagerovic, N. & Elguero, J. (1997). *Tetrahedron*, **53**, 11645–11658.
Takusagawa, F., Higuchi, T., Shimada, A., Tamura, C. & Sasada, Y. (1974). *Bull. Chem. Soc. Jpn*, **47**, 1409–1413.
Takusagawa, F., Hirotsu, K. & Shimada, A. (1973). *Bull. Chem. Soc. Jpn*, **46**, 2020–2027.
Takusagawa, F. & Shimada, A. (1976). *Acta Cryst.* B**32**, 1925–1927.
Wright, W. B. & King, G. S. D. (1953). *Acta Cryst.* **6**, 305–317.