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3-Cyano-4,6-dimethyl-2-pyridone (Guareschi pyridone)

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Key indicators

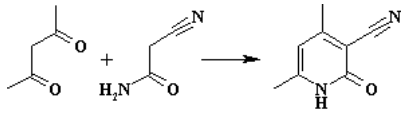
Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.003 Å
R factor = 0.047
wR factor = 0.138
Data-to-parameter ratio = 13.0

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

In the crystal structure of the title compound, $C_8H_8N_2O$, the molecules form centrosymmetric dimers *via* N—H···O hydrogen bonds.

Comment

The 'Guareschi pyridone' (3-cyano-4,6-dimethyl-2-pyridone), (3), has been known for more than a century (Guareschi, 1899). Surprisingly, an analysis of its crystal structure has never been performed. The title compound, (3), was prepared according to the classical scheme:



(1) (2) (3)

The six-membered heterocycle has a well defined diene-like structure; the bond distances C3—C4 and C5—C6 are shorter than the bonds C2—C3 and C4—C5 by more than 3 s.u.

A search of the Cambridge Structural Database (CSD; Version of November 2002; Allen, 2002) gives very few hits for 4,6-disubstituted 3-cyano-2-pyridones. Among these are 3-cyano-6-phenyl-4-trifluoromethyl-2-pyridone (Mishnev *et al.*, 1986) and 3-cyano-6-methyl-2-pyridone (Munakata *et al.*, 1996). The rigid cyano group has the standard linear structure, the bond distance, C31≡N31 of 1.130 (3) Å, in compound (3) being shorter by 0.01 Å than the C≡N bond length in the two above-mentioned pyridones. The C—C bonds of methyl groups C4—C41 [1.502 (3) Å] and C6—C61 [1.504 (3) Å] are almost equal in length. The latter is longer than the bond distance C6—Ph (1.475 Å) in 3-cyano-6-phenyl-4-trifluoromethyl-2-pyridone (Mishnev *et al.*, 1986); this can be explained by conjugation between the phenyl and pyridine rings.

The N1—H1···O2 intermolecular hydrogen bond links the molecules in the crystal structure into centrosymmetric dimers (Fig. 2 and Table 2).

The formation of such centrosymmetric dimers, through intermolecular hydrogen bonding, seems to be typical of 2-pyridones in the crystalline state (Cody, 1987; Dorigo *et al.*, 1993; Mishnev *et al.*, 1986; Munakata *et al.*, 1996).

Experimental

Cyanoacetamide [$NCCH_2C(O)NH_2$] (33.98 g, 0.40 mol), (2), was dissolved in a solution of $NaHCO_3$ (33.98 g, 0.40 mol) in 200 ml of H_2O at 323–333 K. Acetylacetone [$CH_3C(O)CH_2C(O)CH_3$] (40.45 g, 0.40 mol), (1), was added to this solution with vigorous stirring. The colour of the mixture turned yellow and then red, and 3-cyano-4,6-dimethyl-2-pyridone, (3), started to precipitate after 5–7 min. The mixture was allowed to stand overnight, the product filtered, washed

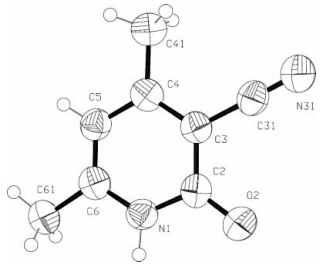


Figure 1
ORTEP-3 (Farrugia, 1997) plot of the molecule of the title compound. Displacement ellipsoids are drawn at the 50% probability level. H atoms are shown as spheres of arbitrary radii.

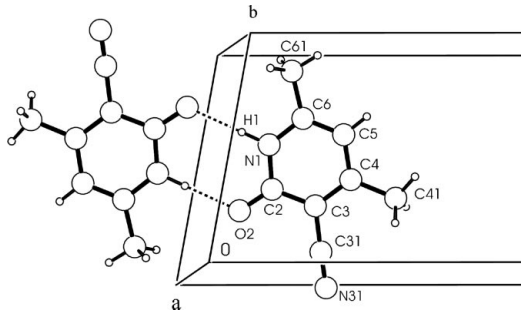


Figure 2
*PLUTON*97 (Spek, 1997) diagram, showing the hydrogen bonds as dashed lines.

with cold water (3 × 150 ml), and dried (yield: 58.16 g, 97%). The product was recrystallized from C_2H_5OH; m.p. 563–565 K. Literature m.p. 563 K (Alberola *et al.*, 1999). ^{1}H NMR ($CDCl_3$, 400 MHz, p.p.m.): 6.10 (*s*, 1H, 5H), 2.45 (3H, *s*, 4-CH_3), 2.40 (3H, *s*, 6-CH_3). The ^{1}H NMR spectrum of (3) was recorded on a Bruker AMX-400.

Crystal data

$C_8H_8N_2O$
M_r = 148.16
Triclinic, $P\overline{1}$
a = 3.975 (4) Å
b = 7.417 (4) Å
c = 12.820 (8) Å
α = 76.36 (4)°
β = 88.54 (4)°
γ = 88.62 (4)°
V = 367.1 (5) Å^3
Z = 2
D_x = 1.340 Mg m^{-3}
Cu $K\alpha$ radiation
Cell parameters from 25 reflections
θ = 22.5–27.0°
μ = 0.75 mm^{-1}
T = 293 (2) K
Cube, colourless
0.30 × 0.30 × 0.30 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
Non-profiled ω scans
Absorption correction: none
1439 measured reflections
1377 independent reflections
924 reflections with $I > 2\sigma(I)$
R_{int} = 0.047
θ_{max} = 69.9°
$h = -4 \rightarrow 4$
$k = -8 \rightarrow 9$
$l = 0 \rightarrow 15$
1 standard reflection every 200 reflections
frequency: 60 min
intensity decay: 1%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.047
$wR(F^2)$ = 0.138
S = 1.08
1377 reflections
106 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0689P)^2 + 0.0196P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.13 e Å^{-3}
$\Delta\rho_{min}$ = −0.12 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

N1—C6	1.351 (2)	C3—C31	1.445 (3)
N1—C2	1.389 (2)	C31—N31	1.130 (3)
N1—H1	0.93 (2)	C4—C5	1.411 (3)
C2—O2	1.235 (2)	C4—C41	1.502 (3)
C2—C3	1.432 (3)	C5—C6	1.358 (3)
C3—C4	1.388 (3)	C6—C61	1.504 (3)
C6—N1—C2	125.03 (16)	N31—C31—C3	178.69 (19)
C6—N1—H1	117.2 (13)	C3—C4—C5	118.54 (17)
C2—N1—H1	117.7 (13)	C3—C4—C41	121.13 (17)
O2—C2—N1	120.56 (17)	C5—C4—C41	120.33 (17)
O2—C2—C3	125.83 (18)	C6—C5—C4	119.63 (17)
N1—C2—C3	113.62 (15)	N1—C6—C5	120.46 (18)
C4—C3—C2	122.72 (17)	N1—C6—C61	115.58 (17)
C4—C3—C31	120.59 (16)	C5—C6—C61	123.96 (18)
C2—C3—C31	116.67 (16)		

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···O2^{i}	0.93 (2)	1.89 (2)	2.810 (3)	171 (2)

Symmetry code: (i) $1-x, 1-y, -z$.

The H atom bonded to N was refined isotropically. H atoms bonded to C atoms were included in calculated positions and refined as riding, with Csp^2—H = 0.93 Å and Csp^3—H = 0.96 Å. For methyl H atoms, U_{iso} values were set equal to $1.5U_{eq}$ of the carrier atom; for other H atoms, U_{iso} values were set equal to $1.2U_{eq}$ of the carrier atom.

Data collection: *CAD*-4 *EXPRESS* (Enraf–Nonius, 1994); cell refinement: *CAD*-4 *EXPRESS*; data reduction: *XCAD*4 (Harms & Wocadlo, 1995); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 *for Windows* (Farrugia, 1997) and *PLUTON*97 (Spek, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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