Acta Cryst. (1985). C**41**, 135–136

Structure of 3,4-Dimethyl-1-(2-pyridyl)pyrano[2,3-*c*]pyrazol-6(1*H*)-one, $C_{13}H_{11}N_3O_2$

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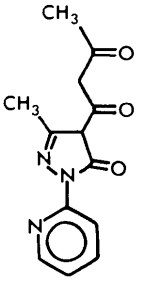
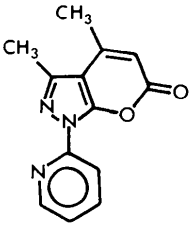
(*Received* 15 *June* 1984; *accepted* 18 *September* 1984)

Abstract. $M_r = 241{\cdot}25$, monoclinic, $C2/c$, $a = 14{\cdot}081$ (4), $b = 17{\cdot}781$ (4), $c = 9{\cdot}828$ (3) Å, $\beta = 112{\cdot}91$ (2)°, $V = 2267$ Å^3, $Z = 8$, $D_m = 1{\cdot}39$ (1), $D_x = 1{\cdot}41$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 0{\cdot}92$ cm^{-1}, $F(000) = 1008$, $T = 293$ K, final $R = 0{\cdot}043$ for 1235 observed reflections. No significant deviation from planarity is observed in the pyranopyrazole system, which is inclined to the pyridine at an angle of 19·0 (4)°. The 4-methyl C atom lies slightly out of the pyranopyrazole mean plane. All intermolecular contacts are >3·2 Å.



(I)



(II)

Introduction. In spite of being known for a long time (Stolle, 1905) pyrano[2,3-*c*]pyrazol-6-ones had received little attention in the literature until recent studies revealed their biological activity (Ueda, Mase, Oda & Ito, 1981; Kuo, Huang & Nakamura, 1984). For example, derivatives of this class have been shown to have antihypertensive, hypoglycemic, vasodilating and analgesic activities. Similarly the isomeric pyrano-[2,3-*c*]pyrazol-4-ones have recently been actively studied and found to be antirheumatic, antiallergic and antitumor agents (Munakata, Naka, Mariwaki & Goto, 1980).

As part of a study of the tautomerism of heterocyclic compounds (Steel & Whyte, 1984; Ramsay & Steel, 1984, unpublished results) the synthesis of the substituted pyrazolone (I) from dehydroacetic acid (*cf.* Gelin, Chantegrel & Nadi, 1983) was undertaken. In the course of this work a minor product was isolated which was thought to be the title compound (II). Its identity was confirmed by independent synthesis from ethyl acetoacetate and 2-hydrazinopyridine (Huang, Kuo & Li, 1979). We now report the first crystal-structure determination of a member of this potentially important class of compounds.

Experimental. Orange crystal, 0·6 × 0·3 × 0·2 mm, from acetonitrile. D_m by flotation (aqueous potassium iodide solution). Nicolet *R*3*m* automated four-circle diffractometer, graphite-monochromated Mo $K\alpha$, lattice parameters from 25 reflections in range $24 < 2\theta < 28°$; $2\theta_{max} = 48°$, standard reflections (no change) 800, 080, 004; 1790 unique reflections measured, 1235 with $I > 3\sigma(I)$ used in refinement, h −15→14, k 0→20, l 0→11, no absorption correction. Direct methods, blocked-cascade least-squares refinement, all non-H atoms anisotropic, H atoms included in calculated positions with isotropic thermal parameters equal to isotropic equivalent of their carrier atoms (C—H 0·96 Å) with methyl H atoms in the conformation deduced from a difference Fourier map; 163 parameters refined on F magnitudes, $R = 0{\cdot}043$, $wR = 0{\cdot}059$, $w = [\sigma^2(F) + 0{\cdot}0013F^2]^{-1}$, $S = 1{\cdot}28$, max. $(\Delta/\sigma) = 0{\cdot}035$ (overall scale), av. $(\Delta/\sigma) = 0{\cdot}006$, $\Delta\rho = -0{\cdot}20$ to $+0{\cdot}16$ e Å^{-3}. All calculations on a Nova 4X computer using *SHELXTL* (Sheldrick, 1983), atomic scattering factors from *International Tables for X-ray Crystallography* (1974).

Discussion. Positional parameters and equivalent isotropic thermal parameters for the non-H atoms are listed in Table 1.* Bond lengths and angles are in Table 2. Fig. 1 shows a perspective view of the molecule and includes the atom labeling.

The pyranopyrazole ring system is planar [r.m.s. deviation 0·009 Å; max. deviation C(4), 0·017 (4) Å]. Of the atoms directly attached, C(4*M*) lies slightly out of plane [deviation 0·110 (4) Å]. The pyridine ring is planar (r.m.s. deviation 0·004 Å) and inclined to the pyranopyrazole mean plane at an angle of 19·0 (4)°.

† Christine Ramsay died tragically following a climbing accident on 28 October 1984.

* Lists of structure factors, anisotropic thermal parameters and H-atom coordinates have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39751 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Rotation of the pyridine ring about the C(2′)—N(1) bond to bring N(1′) and N(2) *syn*-coplanar produces a calculated N(1′)···N(2) interatomic distance of 2·66 Å suggesting a potential capability of bidentate chelation to metal ions.

As shown in Fig. 2 the molecules pack in parallel layers along **a** with all intermolecular distances between non-H atoms >3·2 Å.

Table 1. *Atom coordinates* (×10⁴) *and equivalent isotropic temperature factors* (Å² ×10³) *with e.s.d.'s in parentheses*

	x	*y*	*z*	U_{eq}*
N(1)	3597 (2)	3056 (1)	1860 (2)	45 (1)
N(2)	3839 (2)	3439 (1)	802 (2)	52 (1)
C(3)	4029 (2)	2907 (2)	−4 (3)	49 (1)
C(3a)	3927 (2)	2177 (1)	509 (2)	44 (1)
C(4)	4057 (2)	1412 (2)	152 (3)	51 (1)
C(5)	3855 (2)	877 (2)	982 (3)	57 (1)
C(6)	3562 (2)	1028 (2)	2195 (3)	55 (1)
O(7)	3464 (1)	1790 (1)	2533 (2)	48 (1)
C(7a)	3643 (2)	2310 (1)	1671 (2)	42 (1)
C(3*M*)	4303 (2)	3122 (2)	−1270 (3)	65 (1)
C(4*M*)	4430 (2)	1221 (2)	−1035 (3)	65 (1)
O(6)	3408 (2)	581 (1)	3006 (2)	73 (1)
N(1′)	2917 (2)	3113 (1)	3669 (2)	52 (1)
C(2′)	3401 (2)	3481 (1)	2953 (2)	45 (1)
C(3′)	3707 (2)	4222 (2)	3201 (3)	56 (1)
C(4′)	3492 (2)	4603 (2)	4265 (3)	63 (1)
C(5′)	2994 (2)	4243 (2)	5034 (3)	60 (1)
C(6′)	2733 (2)	3504 (2)	4712 (3)	55 (1)

* Equivalent isotropic *U* defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 2. *Bond lengths* (Å) *and angles* (°) *with e.s.d.'s in parentheses*

N(1)—N(2)	1·391 (3)	N(1)—C(7a)	1·346 (3)
N(1)—C(2′)	1·425 (3)	N(2)—C(3)	1·325 (4)
C(3)—C(3a)	1·420 (4)	C(3)—C(3*M*)	1·489 (4)
C(3a)—C(4)	1·434 (4)	C(3a)—C(7a)	1·369 (4)
C(4)—C(5)	1·352 (4)	C(4)—C(4*M*)	1·493 (4)
C(5)—C(6)	1·432 (5)	C(6)—O(7)	1·413 (3)
C(6)—O(6)	1·203 (4)	O(7)—C(7a)	1·342 (3)
N(1′)—C(2′)	1·328 (4)	N(1′)—C(6′)	1·346 (4)
C(2′)—C(3′)	1·379 (4)	C(3′)—C(4′)	1·376 (4)
C(4′)—C(5′)	1·373 (5)	C(5′)—C(6′)	1·367 (4)
N(2)—N(1)—C(7a)	109·9 (2)	N(2)—N(1)—C(2′)	118·7 (2)
C(7a)—N(1)—C(2′)	131·4 (2)	N(1)—N(2)—C(3)	105·3 (2)
N(2)—C(3)—C(3a)	111·6 (2)	N(2)—C(3)—C(3*M*)	119·6 (2)
C(3a)—C(3)—C(3*M*)	128·8 (3)	C(3)—C(3a)—C(4)	137·7 (3)
C(3)—C(3a)—C(7a)	104·0 (2)	C(4)—C(3a)—C(7a)	118·3 (2)
C(3a)—C(4)—C(5)	116·3 (3)	C(3a)—C(4)—C(4*M*)	121·6 (3)
C(5)—C(4)—C(4*M*)	122·1 (3)	C(4)—C(5)—C(6)	124·5 (3)
C(5)—C(6)—O(7)	117·5 (2)	C(5)—C(6)—O(6)	127·8 (3)
O(7)—C(6)—O(6)	114·8 (3)	C(6)—O(7)—C(7a)	116·9 (2)
N(1)—C(7a)—C(3a)	109·3 (2)	N(1)—C(7a)—O(7)	124·2 (2)
C(3a)—C(7a)—O(7)	126·5 (2)	C(2′)—N(1′)—C(6′)	116·1 (2)
N(1)—C(2′)—N(1′)	115·3 (2)	N(1)—C(2′)—C(3′)	120·1 (3)
N(1′)—C(2′)—C(3′)	124·6 (3)	C(2′)—C(3′)—C(4′)	117·3 (3)
C(3′)—C(4′)—C(5′)	120·0 (3)	C(4′)—C(5′)—C(6′)	118·1 (3)
N(1′)—C(6′)—C(5′)	124·0 (3)		

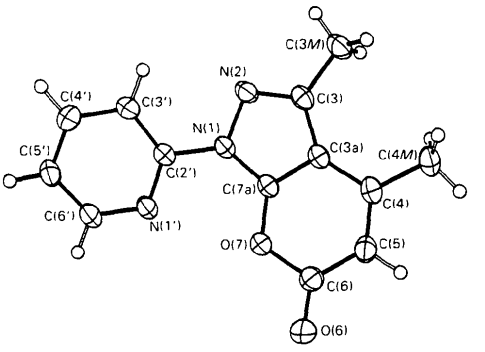

Fig. 1. Perspective view and atom labeling of the title compound.

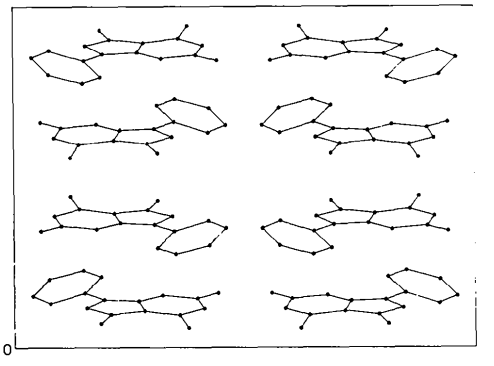

Fig. 2. Unit-cell contents projected along **c** (*a* vertical; *b* horizontal). H atoms omitted for clarity.

We wish to acknowledge grants from the Research Committee of the New Zealand Universities Grants Committee.

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