We are indebted to Dr Doyle Britton at the University of Minnesota for obtaining diffractometer data.

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Acta Cryst. (1993). C**49**, 338–340

Structure of 6-(3,3-Dimethyl-2-oxo-2,3-dihydro-5-furanyl)-2-pyridone at 145 K

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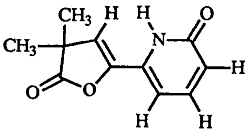
(*Received* 3 *February* 1992; *accepted* 20 *May* 1992)

Abstract. $C_{11}H_{11}NO_3$, $M_r = 205.21$, triclinic, $P\bar{1}$, $a = 5.725\,(1)$, $b = 9.038\,(1)$, $c = 10.401\,(2)$ Å, $\alpha = 101.37\,(1)$, $\beta = 102.63\,(1)$, $\gamma = 102.83\,(1)°$, $V = 494.7\,(3)$ Å^3, $Z = 2$, $D_x = 1.38$ g cm^{-3}, $\lambda(\text{Mo } K\alpha) = 0.7107$ Å, $\mu = 0.62$ cm^{-1}, $F(000) = 216$, $T = 145$ K, $R = 0.049$, $wR = 0.063$ for 2386 unique observed reflections. The molecules, which are self-associating in solution, are arranged in the crystal in centrosymmetric dimers joined by N—H···O bonds between the amide functional groups. Analysis of displacement parameters indicates that the furanyl and pyridone groups are independently quite rigid, with the furanyl group librating with respect to the hydrogen-bonded pyridone.

Experimental. The title compound (2) was prepared *via* the methodology described by Ducharme & Wuest (1988) as part of our efforts to synthesize substituted pyridones. The crucial C—C bond formation linking pyridone and lactone precursors and the γ-lactone ring formation were accomplished in one step by the use of tetrakis(triphenylphosphine)palladium. Proton nuclear magnetic resonance studies indicated a self-associating system with a concentration dependence of the lactam N—H chemical shift. A mathematic extrapolation, as described by Chen & Rosenberger (1990), gave a dimerization constant $K = 8$ in chloroform at 294 K.

6-(3,3-Dimethyl-2-oxo-2,3-dihydro-5-furanyl)-2-benzyloxypyridine (1), the precursor to (2), was prepared by stirring a mixture of 2-benzyloxy-6-bromopyridine (Duggan, Grabowski & Russ, 1980) (2.5 g, 0.01 mol), 2,2-dimethylbut-3-ynoic acid (Schexnayder & Engel, 1975) (1.13 g, 0.01 mol), dry triethylamine (15 mL), tetrakis(triphenylphosphine)palladium (0.35 g, 0.3 mmol) and copper(I) iodide (0.1 g, 0.5 mmol) in a sealed thick-walled pressure tube at 353 K, under an atmosphere of argon, for 5 h. The resultant cooled suspension was added to water (120 mL) and extracted with diethyl ether (2 × 70 mL). The combined ethereal extracts were dried (anhydrous magnesium sulfate) and evaporated *in vacuo* to a yellow oil (2.77 g, 94%). Radial chromatography gave (1) in the second fraction with dichloromethane/hexane (1:1) as eluent, as a pale yellow oil (2.12 g, 72%). Crystallization from benzene/hexane gave (1) as white stubby needles (2.0 g, 70%), m.p. 350.6–351.1 K. IR ($CHCl_3$): ν 1803 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 1.43 (*s*, 6H); 5.41 (*s*, 2H); 6.27 (*s*, 2H); 6.78 (*d*, 1H, *J* 8 Hz); 7.31–7.46



(2)

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(*m*, 5H); 7.62 (*t*, 1H, *J* 8 Hz). ^{13}C NMR ($CDCl_3$): δ 24.43 (*q*); 45.08 (*s*); 67.62 (*t*); 112.34 (*d*); 113.42 (*s*); 127.94 (*d*); 128.09 (*d*); 128.47 (*d*); 137.14 (*d*); 139.36 (*d*); 144.29 (*d*); 150.44 (*s*); 163.18 (*s*); 181.76 (*s*). Analysis calculated for $C_{18}H_{17}NO_3$ (295.3): C 73.20; H 5.80; N 4.74%. Analysis found: C 72.96; H 5.84; N 4.83%.

6-(3,3-Dimethyl-2-oxo-2,3-dihydro-5-furanyl)-2-pyridone (2) was prepared by stirring a solution of (1) (1.5 g, 5.33 mmol) in trifluoroacetic acid (25 mL) for 20 h at room temperature. Evaporation of the solvent (*in vacuo*) gave an orange oil. Crystallization from benzene/hexane gave the title compound as white platelets (0.9 g, 82%), m.p. 493 K (dec.). IR ($CHCl_3$): ν 1802, 1653 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 1.45 (*s*, 6H); 6.57 (*s*, 1H); 6.80 (*d*, 1H, *J* 8 Hz); 6.95 (*d*, 1H, *J* 8 Hz); 7.77 (*t*, 1H, *J* 8 Hz). ^{13}C NMR ($CDCl_3$): δ 23.98 (*q*); 45.66 (*s*); 108.81 (*d*); 117.08 (*s*); 119.72 (*s*); 134.99 (*d*); 143.15 (*d*); 143.84 (*d*); 164.53 (*s*); 179.58 (*s*). Analysis calculated for $C_{11}H_{11}NO_3$ (205.2): C 64.38; H 5.40; N 6.83%. Analysis found: C 64.07; H 5.33; N 7.04%.

A very pale-yellow irregular cut crystal of (2) 0.27 × 0.27 × 0.46 mm was used for data collection on a locally automated Picker diffractometer equipped with a variable temperature device (Strouse, 1976) and a graphite monochromator. Unit-cell parameters were determined by least-squares refinement of 25 reflections ($7.56 < 2\theta < 20.13°$). Data were collected using θ–2θ scans of speed 6.0° min^{-1}, to $2\theta_{\max} = 60°$ for the range $-8 < h < 7$, $-12 < k < 12$, $0 < l < 14$. Three standards monitored every 97 reflections gave a maximum intensity variation of 4% from average. 2979 intensities were measured, 2883 were unique data, of which 2386 had $F > 3\sigma(F)$ (497 considered unobserved). Lorentz and polarization corrections were applied, but no absorption correction (μ = 0.62 cm^{-1}).

Table 1. *Positional parameters and equivalent isotropic displacement parameters* (Å^2) *for* (2)

$$U_{\rm eq} = (1/3)\,(U_{11}a^2\mathbf{a}^{*2} + U_{22}b^2\mathbf{b}^{*2} + U_{33}c^2\mathbf{c}^{*2} + 2U_{12}ab\mathbf{a}^*\mathbf{b}^*\cos\gamma + 2U_{13}ac\mathbf{a}^*\mathbf{c}^*\cos\beta + 2U_{23}bc\mathbf{b}^*\mathbf{c}^*\cos\alpha).$$

	x	*y*	*z*	$U_{\rm eq}$
N1	0.18627 (20)	0.86028 (13)	0.47144 (11)	0.0194 (2)
C2	0.16018 (25)	0.91758 (16)	0.35781 (13)	0.0193 (2)
C3	−0.08587 (25)	0.86850 (16)	0.26620 (13)	0.0202 (2)
C4	−0.27583 (25)	0.77012 (16)	0.29180 (14)	0.0217 (3)
C5	−0.23755 (26)	0.71094 (17)	0.40869 (14)	0.0216 (3)
C6	−0.00415 (25)	0.76023 (16)	0.49782 (13)	0.0191 (2)
O7	0.34280 (19)	1.00708 (13)	0.34007 (10)	0.0265 (2)
O1′	−0.13092 (18)	0.59026 (12)	0.63594 (10)	0.0232 (2)
C2′	−0.05234 (25)	0.56669 (17)	0.76325 (14)	0.0208 (3)
C3′	0.18463 (24)	0.69505 (16)	0.84528 (13)	0.0192 (2)
C4′	0.23851 (25)	0.77820 (16)	0.73956 (13)	0.0201 (2)
C5′	0.05194 (25)	0.71668 (16)	0.62578 (14)	0.0193 (2)
C6′	0.38722 (27)	0.62356 (18)	0.90501 (15)	0.0268 (3)
C7′	0.12173 (31)	0.79942 (19)	0.96092 (16)	0.0304 (3)
O8′	−0.16681 (20)	0.46039 (13)	0.79612 (11)	0.0293 (2)

Table 2. *Distances* (Å) *and angles* (°) *for* (2)

N1—C2	1.373 (2)	N1—C6	1.368 (2)	C2—C3	1.434 (2)
C2—O7	1.245 (2)	C3—C4	1.355 (2)	C4—C5	1.416 (2)
C5—C6	1.369 (2)	C6—C5′	1.451 (2)	O1′—C2′	1.376 (2)
O1′—C5′	1.406 (2)	C2′—C3′	1.523 (2)	C2′—O8′	1.191 (2)
C3′—C4′	1.497 (2)	C3′—C6′	1.525 (2)	C3′—C7′	1.536 (2)
C4′—C5′	1.332 (2)	N1···O7$^{\rm i}$	2.806 (2)	H1···O7$^{\rm i}$	1.82

C2—N1—C6	123.8 (1)	N1—C2—C3	115.7 (1)
N1—C2—O7	120.2 (1)	C3—C2—O7	124.2 (1)
C2—C3—C4	120.9 (1)	C3—C4—C5	121.2 (1)
C4—C5—C6	118.0 (1)	N1—C6—C5	120.4 (1)
N1—C6—C5′	116.9 (1)	C5—C6—C5′	122.7 (1)
C2′—O1′—C5′	107.2 (1)	O1′—C2′—C3′	109.4 (1)
O1′—C2′—O8′	121.2 (1)	C3′—C2′—O8′	129.4 (1)
C2′—C3′—C4′	101.1 (1)	C2′—C3′—C6′	110.6 (1)
C2′—C3′—C7′	107.9 (1)	C4′—C3′—C6′	114.7 (1)
C4′—C3′—C7′	112.3 (1)	C6′—C3′—C7′	109.8 (1)
C3′—C4′—C5′	109.0 (1)	C6—C5′—O1′	114.6 (1)
C6—C5′—C4′	132.5 (1)	O1′—C5′—C4′	112.8 (1)
N1—H1···O7$^{\rm i}$	171		

Symmetry code: (i) $1.0 - x$, $2.0 - y$, $1.0 - z$.

The structure was solved by direct methods using *SHELXS*86 (Sheldrick, 1990). All atoms (including H atoms) were located on Fourier and difference Fourier maps. Refinement included anisotropic thermal parameters for all non-H atoms. H atoms were refined as riding or in rigid methyl groups with C—H restrained to 1.08 and N—H to 1.00 Å, with displacement parameters for H atoms calculated from the *U* value of the attached C or N atom. Refinement was by full-matrix least-squares procedures based on *F* (Sheldrick, 1976) with a maximum $\sin\theta/\lambda$ = 0.70 Å^{-1}. Refinement of 142 parameters converged to $R = 0.049$, $wR = 0.063$ $\{w = 1/\sigma^2\,(F_{\rm obs})$ where $\sigma(F_{\rm obs}) = [|I| + \sigma(I)]^{1/2} - |I|^{1/2}\}$, $S = 1.95$. The ratio of maximum least-squares shift to e.s.d. was 0.029 and the average ratio of shift to e.s.d. was 0.005. Maximum and minimum heights of 0.41 and −0.31 e Å^{-3} in the final difference Fourier synthesis were observed. Atomic scattering factors were obtained from *International Tables for X-ray Crystallography* (1974, Vol. IV). All calculations were performed on a UCLA Departmental DEC VAX 3100. Programs used: the *UCLA Crystallographic Package* (1984) including locally edited versions of *CARESS*, *PROFILE* and *ORTEP*; *SHELXS*86 (Sheldrick, 1990); *SHELX*76 (Sheldrick, 1976).

Atomic coordinates and equivalent isotropic temperature factors for non-H atoms are listed in Table 1 and bond lengths and angles for these atoms are given in Table 2.* An *ORTEP* (Johnson, 1965) drawing is shown in Fig. 1 with the atom-numbering scheme. Fig. 2 is a stereoscopic view of the dimer, showing the N—H···O linkages between monomers.

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* Lists of atomic positions and anisotropic displacement parameters, torsion angles, least-squares planes, thermal-motion analysis results, bond lengths, hydrogen-bond geometry for (2) and for comparable compounds retrieved from the Cambridge Structural Database, and observed and caulated structure factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55462 (23 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: ST1000]

Related literature. Molecular and intermolecular geometry resembles that in related compounds, as determined by a search of the Cambride Structural Database, version 4.5 (Allen, Kennard, Watson, Brammer, Orpen & Taylor, 1987). For the distances in the γ-lactone ring, comparison may be made with the two bifuranylidenedione structures (Begley, Crombie, Griffiths, Jones & Rahmani, 1981). The bond lengths for the pyridone moiety may be compared with those in mamanine dihyrate (Kadooka, Chang, Fukami, Scheuer, Clardy, Solheim & Springer, 1976), in D-glucono-1,5-lactam (Ogura, Furuhata, Takayanagi, Tsuzuno & Iitaka, 1984) and in the two isomers of dipyridonyl ethyne (Ducharme & Wuest, 1988). The geometry of the hydrogen bonding between pyridone rings agrees well with that of similar dimers (see Fig. 2 and Table 3); it is common in N—H···O for the N—H vector to be oriented approximately in the direction of the lone pair expected for an sp^2 O atom (Taylor, Kennard & Versichel, 1983).

Each molecule is composed of two fairly rigid moieties. An analysis of displacement parameters (Dunitz, Schomaker & Trueblood, 1988) gives evidence of rigidity: the average difference in mean-square displacement amplitude between ring atoms is 1×10^{-3} Å^2 (comparable to the r.m.s. standard deviation of $U_{\rm obs}$, 6×10^{-4} Å^2). Good agreement is obtained for a model in which the lactone ring is librating with respect to the pyridone with an amplitude of 12 (3) deg^2 and the attached atoms O7, O8′, C6′ and C7′ are ‘riding’.

Table 3. *Comparison of hydrogen-bonding geometries* (Å, °) *in aromatic lactam dimer fragments*

	N···O	O═C	O═C—N	C—N···O	C═O···N
Average of 13 fragments*	2.824	1.233	121.3	113.8	124.4
E.s.d.	0.053	0.012	1.7	2.1	2.0
This work	2.806	1.245	120.2	113.4	126.1

* A complete tabulation for all 13 fragments and Cambridge Structural Database references are available (see deposition footnote).

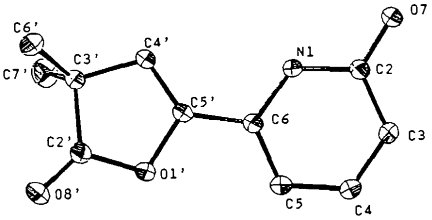

Fig. 1. *ORTEP* (Johnson, 1965) view of (2) showing atomic numbering; atoms in the lactone moiety are primed. Ellipsoids enclose 50% probability; H atoms have been omitted. The normal to the plane of the lactone ring makes an angle of 18° with that of the pyridone plane.

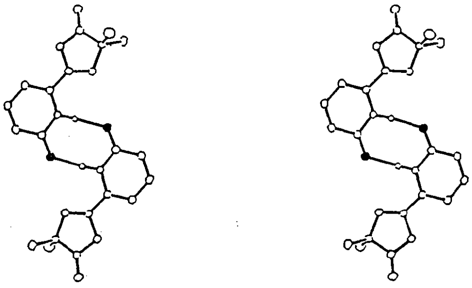

Fig. 2. Stereoview of the centrosymmetric dimer; O atoms have been darkened. The geometry of the hydrogen bonds joining the two molecules is similar to that in 13 closely related fragments; see Table 3.

The authors wish to thank Ming Fun Warasopun for technical assistance. This work was supported by the National Institutes of Health (HD17779).

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