Structure of Diethyl 2,6-Dimethyl-4-[5-(4-methylphenyl)-2-furyl]-1,4-dihydropyridine-3,5-dicarboxylate

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Abstract. $C_{24}H_{27}NO_5$, $M_r = 409.5$, orthorhombic, $Pna2_1$, $a = 12.843$ (4), $b = 17.768$ (4), $c = 9.960$ (3) Å, $V = 2272$ (1) Å^3, $Z = 4$, $D_m = 1.16$ (1), $D_x = 1.197$ Mg m^{-3}, λ(Cu Kα) = 1.54178 Å, $\mu = 0.65$ mm^{-1}, $F(000) = 872$, $T = 293$ K, final $R = 0.043$ for 1699 unique observed reflections. The substituted 1,4-dihydropyridine ring has a flat-boat conformation with the N(1) and C(4) atoms displaced by 0.173 (1) and 0.413 (2) Å, respectively, from the base of the boat. The phenyl group is in conjugation with the furan ring (dihedral angle 6.4°) and this π system is nearly perpendicular to the least-squares plane of the dihydropyridine ring. The molecules are linked by an intermolecular hydrogen bond between N(1)—H and O(9) $(x - \frac{1}{2}, \frac{1}{2} - y, z)$[N···O 2.970 (2) Å].

Experimental. Transparent needles, crystal size 0.1 × 0.15 × 0.5 mm. D_m by flotation in bromoform/*n*-octane. Systematic absences: $0kl$ for $k + l$ odd and $h0l$ for h odd. Syntex $P2_1$ diffractometer, graphite-monochromated Cu Kα radiation. Choice of unit-cell parameters verified by program *UB* (Sivý, Sivý & Koreň, 1987); refinement by least squares on the basis of 15 independent 2θ values in the range 35–52°. Intensity data ($h = 0$ to 15, $k = 0$ to 20, $l = 0$ to 11) by $\theta/2\theta$ scans, scan width 2° plus α-doublet

splitting, $2\theta_{max} = 130°$. Three standards (600, 040 and 002) measured every 100 reflections, no systematic fluctuation. 2059 unique reflections, 1699 with $I \geq 2\sigma(I)$ considered observed and included in the refinement. Data reduction (no absorption or extinction corrections) by using program *XP21* (Pavelčik, 1987). Structure solved by direct methods using *MULTAN80* (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980) and *MAGEX* (Hull, Viterbo, Woolfson & Zhang, 1981) and refined by block-diagonal least squares with anisotropic thermal parameters for non-H atoms. C(18) disordered in two positions with occupancy factors fixed at 0.60 [C(181)] and 0.40 [C(182)], based on relative heights in a difference Fourier map. All H atoms, except those affected by disorder, located from maps and refined isotropically. In final cycle $R = 0.043$, $wR = 0.076$ for observed reflections only, $S = 1.55$, max. shift/e.s.d. 0.15, function minimized $\sum w(\Delta F)^2$, where $w = [\sigma^2(I) + (0.02F_o^2)^2]^{-1/2}$. Max. and min. heights in final $\Delta\rho$ synthesis 0.11 and -0.12 e Å^{-3}. Scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV). All calculations except *UB*, *XP21*, *MULTAN* and *MAGEX* performed with a local version of the *NRC* system (Ahmed, Hall, Pippy & Huber, 1973).

Table 1. Final atomic coordinates ($\times 10^4$), with e.s.d.'s in parentheses, and equivalent isotropic thermal parameters (Å^2)

$$B_{eq} = (4/3)\Sigma_i\Sigma_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}
N(1)	1127 (1)	1952 (1)	−620 (2)	5·02
C(2)	1389 (1)	1832 (1)	703 (2)	5·33
C(3)	2318 (1)	2085 (1)	1160 (2)	5·24
C(4)	3104 (1)	2378 (1)	144 (2)	4·74
C(5)	2559 (1)	2751 (1)	−1023 (2)	4·71
C(6)	1610 (1)	2474 (1)	−1414 (2)	4·69
C(7)	1017 (1)	2653 (1)	−2671 (2)	5·77
C(8)	3097 (1)	3381 (1)	−1651 (2)	4·95
O(9)	4002 (1)	3545 (1)	−1394 (2)	6·00
O(10)	2540 (1)	3781 (1)	−2507 (2)	6·15
C(11)	3026 (2)	4453 (1)	−3063 (3)	7·34
C(12)	2203 (3)	4825 (2)	−3912 (3)	10·22
C(13)	567 (2)	1434 (1)	1488 (3)	7·42
C(14)	2597 (2)	2056 (2)	2592 (3)	7·81
O(15)	2073 (2)	1823 (2)	3481 (2)	15·33
O(16)	3535 (1)	2330 (1)	2828 (2)	9·07
C(17)	3992 (2)	2265 (2)	4192 (4)	11·35
C(181)	3918 (5)	2956 (4)	4778 (7)	14·52
C(182)	4759 (10)	1796 (7)	4364 (13)	16·65
O(19)	4622 (1)	1550 (1)	399 (1)	5·16
C(20)	3787 (1)	1746 (1)	−372 (2)	4·85
C(21)	3707 (1)	1280 (1)	−1429 (2)	5·78
C(22)	4548 (1)	748 (1)	−1310 (2)	6·16
C(23)	5080 (1)	933 (1)	−191 (2)	5·54
C(24)	6030 (1)	650 (1)	466 (2)	6·24
C(25)	6512 (2)	6 (1)	−32 (3)	8·31
C(26)	7416 (2)	−263 (1)	585 (4)	9·35
C(27)	7868 (2)	96 (1)	1630 (4)	9·12
C(28)	7390 (2)	737 (1)	2105 (4)	9·52
C(29)	6473 (2)	1005 (1)	1541 (4)	7·91
C(30)	8837 (2)	−231 (2)	2287 (6)	13·15

Final atomic coordinates of non-H atoms and equivalent B's are listed in Table 1,* bond distances and angles in Table 2. A perspective drawing of the molecule and numbering of the atoms are shown in Fig. 1.

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

N(1)—C(2)	1·377 (3)	O(10)—C(11)	1·456 (3)
C(2)—C(3)	1·354 (2)	C(11)—C(12)	1·507 (4)
C(3)—C(4)	1·522 (3)	C(4)—C(20)	1·514 (2)
C(4)—C(5)	1·510 (3)	C(20)—O(19)	1·365 (2)
C(5)—C(6)	1·372 (2)	C(20)—C(21)	1·344 (3)
C(6)—N(1)	1·366 (2)	C(21)—C(22)	1·441 (3)
C(2)—C(7)	1·499 (3)	C(22)—C(23)	1·347 (3)
C(2)—C(13)	1·491 (3)	C(23)—O(19)	1·376 (2)
C(3)—C(14)	1·471 (3)	C(23)—C(24)	1·473 (3)
C(14)—O(15)	1·186 (4)	C(24)—C(25)	1·392 (3)
C(14)—O(16)	1·321 (3)	C(25)—C(26)	1·398 (4)
O(16)—C(17)	1·485 (4)	C(26)—C(27)	1·352 (5)
C(17)—C(181)	1·363 (9)	C(27)—C(28)	1·378 (4)
C(17)—C(182)	1·301 (13)	C(28)—C(29)	1·387 (4)
C(5)—C(8)	1·456 (2)	C(29)—C(24)	1·367 (4)
C(8)—O(9)	1·225 (2)	C(27)—C(30)	1·522 (4)
C(8)—O(10)	1·321 (2)		
C(2)—N(1)—C(6)	123·3 (2)	C(3)—C(14)—O(16)	112·4 (2)
N(1)—C(2)—C(3)	119·0 (2)	O(15)—C(14)—O(16)	120·9 (3)
N(1)—C(2)—C(13)	113·7 (2)	C(14)—O(16)—C(17)	119·6 (2)
C(3)—C(2)—C(13)	127·2 (2)	O(16)—C(17)—C(181)	107·1 (4)
C(2)—C(3)—C(4)	118·4 (2)	O(16)—C(17)—C(182)	117·9 (6)
C(2)—C(3)—C(14)	121·9 (2)	C(181)—C(17)—C(182)	125·0 (7)
C(4)—C(3)—C(14)	119·7 (2)	C(20)—O(19)—C(23)	107·4 (1)
C(3)—C(4)—C(5)	110·7 (1)	C(4)—C(20)—O(19)	117·0 (1)
C(3)—C(4)—C(20)	110·9 (1)	C(4)—C(20)—C(21)	132·8 (2)
C(5)—C(4)—C(20)	109·4 (1)	O(19)—C(20)—C(21)	110·1 (2)
C(4)—C(5)—C(6)	118·2 (2)	C(20)—C(21)—C(22)	106·4 (2)
C(4)—C(5)—C(8)	116·6 (2)	C(21)—C(22)—C(23)	106·7 (2)
C(6)—C(5)—C(8)	125·2 (2)	O(19)—C(23)—C(22)	109·3 (2)
N(1)—C(6)—C(5)	118·8 (2)	O(19)—C(23)—C(24)	115·8 (2)
N(1)—C(6)—C(7)	113·4 (2)	C(22)—C(23)—C(24)	134·7 (2)
C(5)—C(6)—C(7)	127·7 (2)	C(23)—C(24)—C(25)	119·3 (2)
C(5)—C(8)—O(9)	122·9 (2)	C(23)—C(24)—C(29)	122·4 (2)
C(5)—C(8)—O(10)	115·7 (2)	C(25)—C(24)—C(29)	118·2 (2)
O(9)—C(8)—O(10)	121·4 (2)	C(24)—C(25)—C(26)	119·6 (2)
C(8)—O(10)—C(11)	117·1 (2)	C(25)—C(26)—C(27)	122·3 (3)
O(10)—C(11)—C(12)	105·8 (2)	C(26)—C(27)—C(28)	117·6 (3)
C(3)—C(14)—O(15)	126·7 (3)	C(26)—C(27)—C(30)	120·1 (3)
		C(28)—C(27)—C(30)	122·2 (3)
		C(27)—C(28)—C(29)	121·5 (3)
		C(24)—C(29)—C(28)	120·8 (3)

Related literature. The flat-boat conformation of the dihydropyridine ring has been previously reported for other compounds incorporating this moiety (Fonseca, Martínez-Carrera & García-Blanco, 1986, and references therein) as well as for closely related 4*H*-pyrans (Sharanina, Nesterov, Klokol, Rodinovskaya, Shklover, Sharanin, Struchkov & Promonenkov, 1986; Klokol, Sharanina, Nesterov, Shklover, Sharanin & Struchkov, 1987). The conjugation between the phenyl and furyl groups, to an even greater extent than in the title compound, has also been observed in the closely related compound ethyl 2-acetyl-3-[5-(4-methylphenyl)-2-furyl]acrylate (dihedral angle 1·3°) (Lokaj, Vrábel, Sivý, Ilavský & Ječný, 1990). As a consequence of the disorder, the C(17)—C(181) and C(17)—C(182) distances appear considerably shortened [1·363 (9) and 1·301 (13) Å, respectively]. Other bond distances and angles within

* Lists of structure factors, anisotropic thermal parameters, H-atom parameters and least-squares planes have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53580 (13 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.
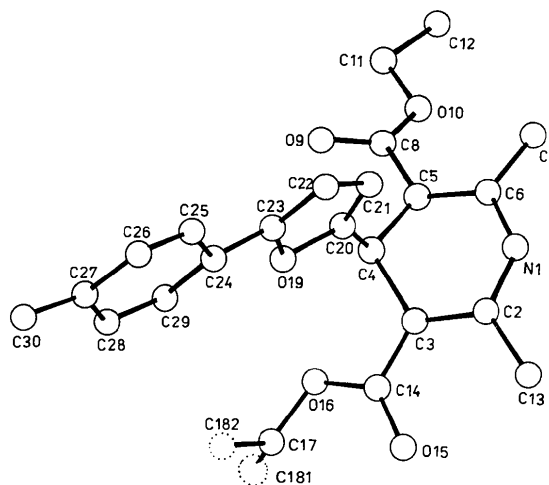

Fig. 1. A perspective view of the title compound showing the atom numbering. C(181) and C(182) are disordered sites for the C(18) methyl carbon. H atoms are not drawn for clarity.

the ethoxycarbonyl groups agree with those systematically observed in these groups (Merlino, 1971; Dunitz & Schweizer, 1982).

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Structure of 3,5-Dihydrobenz[f]indolizin-3-one

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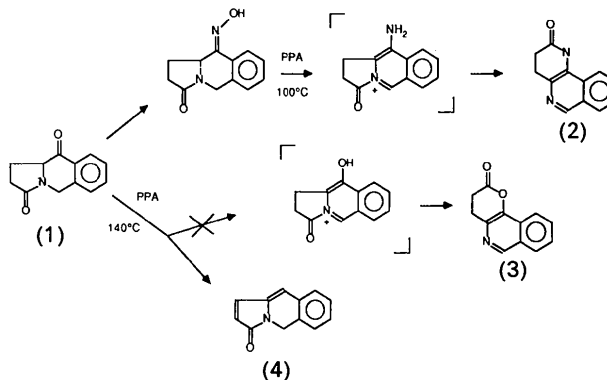
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Abstract. $C_{12}H_9NO$, $M_r = 183.2$, triclinic, $P\bar{1}$, $a = 8.837$ (6), $b = 7.910$ (6), $c = 6.903$ (5) Å, $\alpha = 108.2$ (1), $\beta = 77.7$ (1), $\gamma = 101.4$ (1)°, $V = 443.4$ Å³, $Z = 2$, $D_x = 1.372$ g cm⁻³, Mo $K\alpha$, $\lambda = 0.71069$ Å, $\mu = 0.5$ cm⁻¹, $F(000) = 192$, $T = 293$ (2) K, $R = 0.054$ for 1626 reflections with $I \geq 3\sigma(I)$. Elemental analysis and the mass spectrum of the compound, and one- and two-dimensionally correlated NMR spectra are in good agreement with the results of the structure analysis, in which the molecule is found to be roughly planar.

Experimental. As described in the literature (Rigo & Kolocouris, 1984), fine powder of (1) (1 g, 4·97 mmol) was quickly added to hot (413 K), stirred polyphosphoric acid (20 g). The mixture was vigorously stirred for 1 h. The hot mixture was decanted over crushed ice (150 ml) and the aqueous solution was extracted with dichloromethane. The organic phase was washed with water, dried over K_2CO_3,

filtered and concentrated to give 70% yield of a red powder, which was then treated overnight in dichloromethane at room temperature, with activated carbon, filtered and concentrated in part; pure yellow crystals of (4), which turned red in air, were obtained by slow evaporation of the solvent at 437 K.

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