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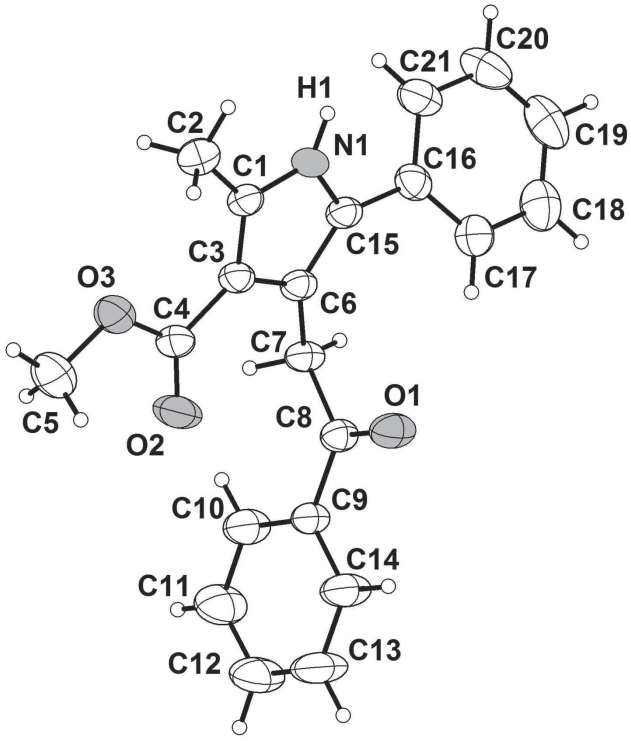
Crystal structure of methyl-2-methyl-4-(2-oxo-2-phenylethyl)-5-phenyl-1*H*-pyrrole-3-carboxylate, $C_{21}H_{19}NO_3$



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Abstract

$C_{21}H_{19}NO_3$, monoclinic, $P2_1/n$ (no. 14), $a = 10.137(2)$ Å, $b = 12.3205(18)$ Å, $c = 14.700(3)$ Å, $\beta = 106.432(1)°$, $V = 1760.9(6)$ Å^3, $Z = 4$, $R_{gt}(F) = 0.0511$, $wR_{ref}(F^2) = 0.1808$, $T = 293$ K.

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The asymmetric unit of the title crystal structure is shown in the figure. Tables 1 and 2 contain details on crystal structure and measurement conditions and a list of the atoms including atomic coordinates and displacement parameters.

Table 1: Data collection and handling.

Crystal:	Colourless prism
Size:	0.20 × 0.20 × 0.20 mm
Wavelength:	Mo $K\alpha$ radiation (0.71075 Å)
μ:	0.8 cm^{-1}
Diffractometer, scan mode:	Rigaku CCD, φ and ω
$2\theta_{max}$, completeness:	55°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	9945, 4030, 0.037
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 2909
$N(param)_{refined}$:	226
Programs:	Sir92 [26], Crystal Structure [27], SHELX [28]

Source of material

Anhydrous $InCl_3$ (22 mg, 10 mmol) and NH_4OAc (85 mg, 1.1 mmol) were added to a mixture of 1,2-dibenzoyl ethylene (1 mmol) and a methyl acetoacetate compound (1 mmol) in dry THF (15 mL). The reaction mixture was stirred at room temperature. After complete disappearance of the starting material (monitored by TLC using methanol/chloroform, 1:9), the solvent was evaporated in a rotary evaporator. The reaction mixture was diluted with water (10 mL) and extracted with $CHCl_3$ (25 mL). The organic layer was separated, washed with brine, and then dried over anhydrous Na_2SO_4. Removal of the solvent resulted in the crude product, which was chromatographed over silica gel using petroleum ether and increasing proportions of chloroform as eluent to get the title compound. The light yellowish crystals of the title compound were obtained by slow evaporation of a solvent solution at room temperature. 319 mg (96%); m.p. 158–160 °C, Rf 0.2 (chloroform/petroleum ether, 3:1). IR (KBr)/cm-1 3249 (N—H), 1702 (C—O), 1658 (C—O), 1446, 1344, 1260, 1220, 1140, 1094. ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 8.40 (br s, NH), 8.06 (d, J = 7.2, 2H, ArH), 7.56 (t, J = 7.6, 1H, ArH), 7.46 (t, J = 8.0, 2H,

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2).

Atom	x	y	z	U_{iso}*/U_{eq}
O1	0.27793(16)	0.25321(10)	1.14220(9)	0.0550(4)
O2	−0.07988(17)	0.27786(11)	1.08119(12)	0.0637(5)
O3	−0.19384(16)	0.37749(11)	1.16108(11)	0.0575(4)
N1	0.14082(16)	0.58495(11)	1.21518(10)	0.0401(4)
C1	0.02765(19)	0.52695(13)	1.21638(12)	0.0388(4)
C2	−0.0593(3)	0.56050(17)	1.27746(15)	0.0535(5)
C3	0.01822(18)	0.44248(13)	1.15224(12)	0.0368(4)
C4	−0.0863(2)	0.35798(14)	1.12689(13)	0.0427(5)
C5	−0.2987(3)	0.2949(2)	1.1419(3)	0.0741(8)
C6	0.13031(18)	0.45162(13)	1.11203(11)	0.0364(4)
C7	0.1487(2)	0.38174(13)	1.03292(12)	0.0391(4)
C8	0.19889(19)	0.26766(13)	1.06336(12)	0.0380(4)
C9	0.15498(19)	0.17520(13)	0.99565(12)	0.0393(4)
C10	0.0592(3)	0.18690(17)	0.90722(14)	0.0571(6)
C11	0.0190(3)	0.09870(19)	0.84799(16)	0.0722(8)
C12	0.0732(3)	−0.00235(19)	0.87543(17)	0.0706(8)
C13	0.1666(4)	−0.01561(17)	0.96217(18)	0.0751(8)
C14	0.2075(3)	0.07227(16)	1.02163(16)	0.0630(7)
C15	0.20615(19)	0.54096(13)	1.15281(12)	0.0371(4)
C16	0.32817(19)	0.59416(15)	1.13870(12)	0.0415(4)
C17	0.4330(2)	0.53439(17)	1.11884(13)	0.0492(5)
C18	0.5490(3)	0.5857(3)	1.10801(16)	0.0635(6)
C19	0.5626(3)	0.6963(3)	1.11660(18)	0.0709(7)
C20	0.4596(3)	0.7563(2)	1.13637(19)	0.0705(7)
C21	0.3427(3)	0.70704(17)	1.14685(16)	0.0573(6)
H1	0.1685	0.6420	1.2490	0.0481*
H2A	−0.1456	0.5878	1.2385	0.0643*
H2B	−0.0131	0.6163	1.3203	0.0643*
H2C	−0.0756	0.4991	1.3131	0.0643*
H5A	−0.3361	0.2864	1.0746	0.0889*
H5B	−0.3706	0.3158	1.1690	0.0889*
H5C	−0.2593	0.2274	1.1692	0.0889*
H7A	0.2140	0.4165	1.0052	0.0469*
H7B	0.0616	0.3770	0.9841	0.0469*
H10	0.0218	0.2549	0.8879	0.0685*
H11	−0.0451	0.1077	0.7891	0.0866*
H12	0.0464	−0.0615	0.8351	0.0848*
H13	0.2027	−0.0840	0.9812	0.0901*
H14	0.2717	0.0623	1.0803	0.0756*
H17	0.4251	0.4593	1.1128	0.0591*
H18	0.6184	0.5449	1.0947	0.0762*
H19	0.6408	0.7304	1.1091	0.0851*
H20	0.4690	0.8313	1.1428	0.0846*
H21	0.2734	0.7488	1.1594	0.0687*

ArH), 7.31, −7.21 (m, 7H, ArH), 4.42 (s, 2H, −C(O)CH_2−), 3.54 (s, 3H, −OCH_3), 2.51 (s, 3H, pyrrole ring 2-CH_3). ^{13}C-NMR (125 MHz, $CDCl_3$) δ: 199.2, 165.9, 137.5, 136.4, 132.8, 132.0, 129.8, 128.8, 128.5, 128.2, 127.3, 127.2, 115.0, 111.6, 50.4, 36.4, 14.0. Anal. Calc. for $C_{21}H_{19}NO_3$: C 75.66, H 5.74, N 4.20. Found: C 75.61, H 5.71, N 4.19%.

Experimental details

The structure was solved by direct method [26] and expanded using Fourier techniques. Carbon-bound hydrogen atoms were placed in calculated positions (C—H = 0.95 Å for aromatic carbon atoms and C—H = 0.99 Å for methylene groups) and were included in the refinement in the riding model approximation, with U_{iso}(H) set to 1.2U_{eq}(C).

Discussion

Tetra-substituted pyrroles were prepared from 1,2-dibenzoyl ethylene and methyl acetoacetate employing NH_4OAc as a nitrogen source, through a combination of Michael addition and Paal–Knorr methods [1–3]. The pyrrole [4–7] ring is one of the most common skeletal features found in heterocycles and natural products [8–10]. Generally, pyrroles possess a broad spectrum of biological activities such as antimicrobial [11], telomerase inhibitory [12], antifungal [13], cardiotonic [14], pheromonal [15], and phytotoxic effects [16]. The classical approaches for synthesizing pyrroles are Knorr [17, 18], Hantzsch [19–21], and Paal-Knorr [1–3] methods. A whole new library of pyrrole derivatives can thus be prepared from commercially available starting materials. Typical examples of such derivatives reported being; Ethyl 2,5-di-tert-butyl-5-ethoxy-4-oxo-4,5-dihydro-1*H*-pyrrole-3-carboxylate [22], Ethyl 1,4-bis(4-chlorophenyl)-2-methyl-1*H*-pyrrole-3-carboxylate [23], Methyl 1-benzyl-5-methyl-2,4-diphenyl-1*H*-pyrrole-3-carboxylate [24] and 4-(3,3,4,4,5,5-hexafluoro-2-(5-(4-methoxyphenyl)-2-methylthiophene-3-yl) cyclopent-1-enyl)-1,5-dimethyl-1*H*-pyrrole-2-carbonitrile [25]. All bond lengths and angle in the title molecule (*cf*. the figure) are in the normal ranges.

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