Crystal structure of ethyl-5-methyl-1-(pyridin-3-yl)-1*H*-pyrazole-4-carboxylate-(dibenzoylmethane), $C_{17}H_{15}N_4O$

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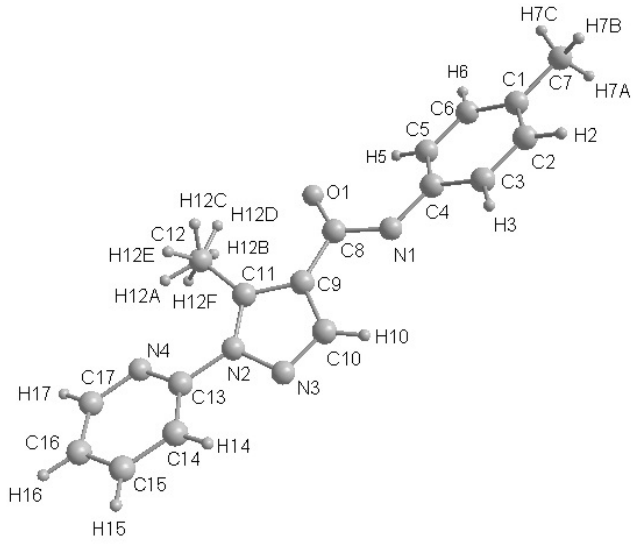

Abstract

$C_{17}H_{15}N_4O$, tetragonal, $I4_1/a$ (no. 88), a = 16.2111(9) Å, c = 22.095(3) Å, V = 5806.6 Å^3, Z = 16, $R_{gt}(F)$ = 0.0479, $wR_{ref}(F^2)$ = 0.1476, T = 296 K.

Table 1. Data collection and handling.

Crystal:	yellow blocks, size 0.18×0.27×0.38 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	0.87 cm^{-1}
Diffractometer, scan mode:	CCD area detector, φ and ω scans
$2\theta_{max}$:	50.98°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	21955, 2703
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 2197
$N(param)_{refined}$:	200
Programs:	SHELXS-97 [13]

Source of material

The title compound was synthesized from ethyl-5-methyl-1-(pyridin-3-yl)-1*H*-pyrazole-4-carboxylate (80 % yield) in form of yellow crystals. To a solution of ethyl 5-methyl-1-(pyridin-3-yl)-1*H*-pyrazole-4-carboxylate (1 mmol) in EtOH 3,5-dimethylbenzenamine (1 mmol) was added. The mixture was then stirred at reflux until the substrate had been consumed completely. After evaporation of the solvent, the residue was purified by SiO_2 gel column chromatography to give 5-methyl-*N*-(3,5-dimethylphenyl)-1-(pyridin-3-yl)-1*H*-pyrazole-4-carboxamide Suitable crystals for a *X*-ray diffraction study were obtained from a chloroform solution [12].

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Experimental details

At the benzene ring the hydrogen atoms were assigned with $U_{iso}(H) = 1.2\ U_{eq}(C)$, and included in the final refinement by using geometrical restraints, with d(C–H) = 0.93 Å. For the methyl group at the benzene ring, the hydrogen atoms were assigned with $U_{iso}(H) = 1.5\ U_{eq}(C)$, and included in the final refinement by using geometrical restraints, with d(C–H) = 0.96 Å.

Discussion

Pyrazole derivatives play an important role in organic chemistry because they have proven to be extremely useful intermediates for the preparation of new biological materials. The pyrazole ring is present in numerous pharmacologically and agrochemically important compounds, such as inhibitors of HIV-1 reverse transcriptase [1], hypocholesterolemic activity [2] and elective inhibition of cyclooxygenase-2 (COX-2) [3]. Several compounds of this type act as antagonists of the receptor, which is present on the surface of many tumor cells [4]. Others are important agrochemicals used, e.g., as insecticides [5]. Of particular importance as a pharmacophore, the N-substituented pyrazole derivatives form part of several drugs such as the antidepressant Zometapine [6], the inhibitor of type 5 cGMP phosphodiesterase Sildenafil [7], and the antibacterial agent FR21818 [8]. Good examples of the usefulness of this same unit in the preparation of insecticides and acaricides include the pesticides Tebufenpyrad [9] Tolfenpyrad [10] and Cyanopyrafen [11]. For these reasons, the efficient synthesis of pyrazole derivatives continues to attract the interest of synthetic chemists. In this context, we report the synthesis of the title compound. The molecule of the title compound shows the pyridine ring, the pyrazole ring and the benzene ring which are approximately planar, but the whole molecule is not. The molecular conformation is characterized by the C8–N1–C4–C3 and N1–C8–C9–C10 torsion angles of 158.81(19)° and -5.3(3)°, which clearly deviate from planarity. Thus, the dihedral angle between the pyrazole ring and the pyridine ring is 17.03°, the dihedral angle between the Pyrazole ring and the benzene ring is 26.51°, and the dihedral angle between the benzene ring and the pyridine ring is 12.07°. In the molecule, the N(1)–C(8), N(1)–C(4), N(2)–C(13), N(3)–C(10), N(4)–C(13), N(2)–N(3) bond lengths are found to be 1.369(2) Å, 1.413(2) Å, 1.425(2) Å, 1.310(2) Å, 1.320(2) Å and 1.3721(19) Å, respectively, which are nearly equal to other typical single bonds. The bond lengths of C(8)–O(1) is found to be 1.231(2) Å, respectively, which is in accordance with a typical double bond. The bond angles C13–N4–C17, C11–N2–N3, C11–N2–C13, N3–N2–C13, N4–C13–N2, O1–C8–C9, N1–C8–C9 and C8–N1–C4 are 116.12(16)°, 112.00(14)°, 131.77(14)°, 116.21(13)°, C13 117.25(15)°, 123.50(16)°, 113.47(15)° and 128.01(15)°. Finally, a stable framework structure is formed by these interactions.

Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	Occ.	*x*	*y*	*z*	U_{iso}
H(2)	16*f*		1.0057	0.5759	–0.1053	0.068
H(3)	16*f*		0.8756	0.5204	–0.1062	0.068
H(5)	16*f*		0.8375	0.6047	0.0619	0.064
H(6)	16*f*		0.9677	0.6603	0.0613	0.067
H(7A)	16*f*		1.0887	0.7105	–0.0398	0.098
H(7B)	16*f*		1.1248	0.6209	–0.0417	0.098
H(7C)	16*f*		1.1066	0.6632	0.0206	0.098
H(10)	16*f*		0.6379	0.4638	–0.0942	0.057
H(12A)	16*f*	0.5	0.5213	0.3775	0.1117	0.080
H(12B)	16*f*	0.5	0.5744	0.4572	0.1213	0.080
H(12C)	16*f*	0.5	0.6177	0.3714	0.1140	0.080
H(12D)	16*f*	0.5	0.6210	0.4266	0.1196	0.080
H(12E)	16*f*	0.5	0.5679	0.3468	0.1100	0.080
H(12F)	16*f*	0.5	0.5245	0.4327	0.1173	0.080
H(14)	16*f*		0.4302	0.3083	–0.0829	0.059
H(15)	16*f*		0.3073	0.2387	–0.0675	0.067
H(16)	16*f*		0.2489	0.2381	0.0287	0.068
H(17)	16*f*		0.3151	0.3057	0.1046	0.074

Table 3. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
O(1)	16*f*	0.73141(8)	0.50209(9)	0.07412(6)	0.0574(8)	0.0671(9)	0.0398(8)	–0.0094(7)	–0.0060(6)	0.0003(6)
N(1)	16*f*	0.76462(9)	0.5166(1)	–0.02589(7)	0.0430(8)	0.060(1)	0.0448(9)	–0.0068(7)	–0.0027(6)	0.0024(7)
N(2)	16*f*	0.51708(9)	0.38992(9)	–0.00513(6)	0.0446(8)	0.0444(8)	0.0289(7)	–0.0006(6)	0.0004(6)	–0.0007(6)
N(3)	16*f*	0.5374(1)	0.4073(1)	–0.06404(6)	0.0548(9)	0.062(1)	0.0298(8)	–0.0086(8)	0.0003(6)	0.0014(6)
N(4)	16*f*	0.4102(1)	0.3470(1)	0.05899(7)	0.059(1)	0.066(1)	0.0379(8)	–0.0129(8)	0.0055(7)	–0.0041(7)
C(1)	16*f*	1.0023(1)	0.6228(1)	–0.02136(9)	0.045(1)	0.050(1)	0.050(1)	–0.0012(8)	–0.0033(8)	0.0058(8)
C(2)	16*f*	0.9724(1)	0.5813(1)	–0.0713(1)	0.057(1)	0.063(1)	0.050(1)	–0.006(1)	0.0114(9)	–0.0064(9)
C(3)	16*f*	0.8942(1)	0.5477(1)	–0.07179(9)	0.058(1)	0.067(1)	0.044(1)	–0.014(1)	0.0018(9)	–0.0103(9)
C(4)	16*f*	0.8432(1)	0.5540(1)	–0.02176(8)	0.0435(9)	0.048(1)	0.0425(9)	0.0012(8)	–0.0039(7)	0.0040(7)
C(5)	16*f*	0.8713(1)	0.5979(1)	0.02823(8)	0.050(1)	0.068(1)	0.042(1)	–0.0048(9)	0.0029(8)	–0.0050(9)
C(6)	16*f*	0.9496(1)	0.6312(1)	0.02760(9)	0.055(1)	0.068(1)	0.044(1)	–0.011(1)	–0.0053(9)	–0.0038(9)
C(7)	16*f*	1.0884(1)	0.6575(2)	–0.0205(1)	0.053(1)	0.074(2)	0.068(1)	–0.012(1)	0.001(1)	–0.001(1)
C(8)	16*f*	0.7138(1)	0.4926(1)	0.02037(8)	0.0434(9)	0.0389(9)	0.042(1)	0.0050(7)	–0.0032(7)	0.0013(7)
C(9)	16*f*	0.6366(1)	0.4534(1)	–0.00056(7)	0.0432(9)	0.0393(9)	0.0369(9)	0.0034(7)	–0.0016(7)	0.0005(7)
C(10)	16*f*	0.6088(1)	0.4449(1)	–0.06066(8)	0.050(1)	0.057(1)	0.0353(9)	–0.0063(8)	0.0033(7)	0.0033(8)
C(11)	16*f*	0.5758(1)	0.4171(1)	0.03453(7)	0.0420(9)	0.0389(9)	0.0334(8)	0.0047(7)	–0.0034(7)	–0.0015(6)
C(12)	16*f*	0.5720(1)	0.4047(1)	0.10132(8)	0.054(1)	0.072(1)	0.034(1)	–0.0050(9)	–0.0041(8)	0.0026(8)
C(13)	16*f*	0.4418(1)	0.3462(1)	0.00395(7)	0.0409(9)	0.0379(8)	0.0353(8)	0.0040(7)	–0.0022(7)	0.0011(7)
C(14)	16*f*	0.4057(1)	0.3069(1)	–0.04487(8)	0.051(1)	0.060(1)	0.0368(9)	–0.0024(9)	–0.0029(8)	–0.0025(8)
C(15)	16*f*	0.3331(1)	0.2660(1)	–0.03561(9)	0.052(1)	0.064(1)	0.051(1)	–0.0067(9)	–0.0115(9)	–0.0043(9)
C(16)	16*f*	0.2983(1)	0.2654(1)	0.0213(1)	0.048(1)	0.062(1)	0.059(1)	–0.0111(9)	–0.0023(9)	0.0069(9)
C(17)	16*f*	0.3386(1)	0.3061(1)	0.0662(1)	0.059(1)	0.081(2)	0.046(1)	–0.018(1)	0.0099(9)	0.001(1)

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