Crystal structure of methyl 4-(methylamino)-3-nitrobenzoate, $C_9H_{10}N_2O_4$

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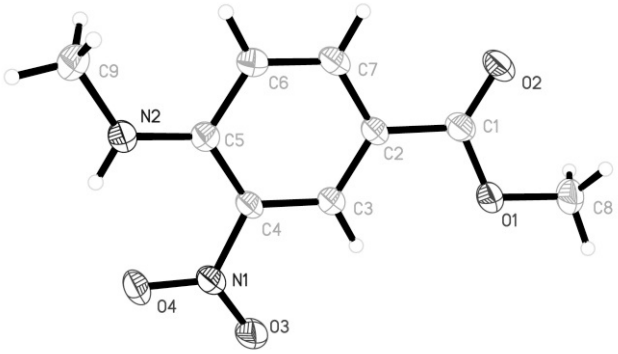

Abstract

$C_9H_{10}N_2O_4$, monoclinic, $P2_1/c$ (no. 14), a = 7.8167(7) Å, b = 8.6045(8) Å, c = 14.321(1) Å, β = 92.758(1)°, V = 962.1 Å^3, Z = 4, $R_{gt}(F)$ = 0.0437, $wR_{ref}(F^2)$ = 0.1140, T = 298 K.

Table 1. Data collection and handling.

Crystal:	yellow blocks, size 0.17×0.35×0.50 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	1.16 cm^{-1}
Diffractometer, scan mode:	SMART 1000 CCD, φ and ω
$2\theta_{max}$:	50.04°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	4865, 1697
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 1153
$N(param)_{refined}$:	136
Programs:	SHELX [5]

Source of material

All reagents and solvents from commercial sources were used without further purification. 4-(methylamino)-3-nitrobenzoic acid (9.0 g, 50 mmol) was added to absolute methanol (100 mL), and then 5 mL of sulfuric acid (mass concentration 98%) were dropped into the solution. Under refluxing the mixture for 8 h, and after cooling and filtration, an orange solid was obtained. The product was recrystallised from THF to give light yellow crystals, m.p.423-424 K.

Experimental details

Refinement of F^2 against all reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2\sigma(F^2)$ is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R- factors based on all data will be even larger.

Discussion

The methyl 4-(methylamino)-3-nitrobenzoate acts as an important precursor for the synthesis of benzamide derivatives which have been reported to possess neuroleptic activities [1, 2]. Herein, we reported its crystal structure. The crystal structure of the title compound is built up by the $C_9H_{10}N_2O_4$ molecules (Figure). The bond lengths of N1–C4 and N2–C9 are 1.446(2)Å and 1.450(2)Å, respectively. All bond lengths are in normal ranges in the title compound [1]. There are N2–H2···O2 hydrogen bonds and weak C7–H7···O4 hydrogen bonds. Their symmetry codes are (1/2 + x, 3/2 - y, -1/2 + z) and (-1/2 + x, 3/2 - y, 1/2 + z), respectively. The benzene ring in the title compound is approximately planar with the nitro group and ester group. The dihedral angles between the benzene ring plane (C2–C3–C4–C5–C6–C7) and the plane of nitro group (O3–O4–N1–C1–C2–C3) and the ester group plane (O1–O2–C1–C2–C8) are 1.27(7)° and 6.83(9)° respectively. In addition, C8–H8A–π interactions with a 2.82Å distance of C8–Cg(1) are found in the compound. The crystal packings are stabilized by these hydrogen bonds and π-interactions.

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

Atom	Site	x	y	z	U_{iso}
H(2)	4*e*	0.8260	0.8941	0.4396	0.060
H(3)	4*e*	0.6726	0.4336	0.5726	0.050
H(6)	4*e*	0.6377	0.9549	0.6470	0.058
H(7)	4*e*	0.5300	0.7737	0.7426	0.058
H(8A)	4*e*	0.5095	0.1909	0.8087	0.093
H(8B)	4*e*	0.4228	0.1111	0.7201	0.093
H(8C)	4*e*	0.3244	0.2400	0.7733	0.093
H(9A)	4*e*	0.6456	1.1148	0.5111	0.089
H(9B)	4*e*	0.8135	1.1446	0.4582	0.089
H(9C)	4*e*	0.8240	1.1123	0.5661	0.089

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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}
N(1)	4*e*	0.8175(2)	0.5877(2)	0.4485(1)	0.062(1)	0.046(1)	0.0393(9)	0.0009(9)	0.0157(8)	–0.0016(9)
N(2)	4*e*	0.7787(2)	0.9222(2)	0.4899(1)	0.063(1)	0.041(1)	0.047(1)	–0.0002(9)	0.0176(8)	0.0031(8)
O(1)	4*e*	0.5064(2)	0.3248(2)	0.69544(9)	0.071(1)	0.046(1)	0.0486(8)	–0.0083(7)	0.0242(7)	0.0017(7)
O(2)	4*e*	0.4491(2)	0.5026(2)	0.8042(1)	0.081(1)	0.061(1)	0.0461(9)	0.0002(8)	0.0301(8)	–0.0004(7)
O(3)	4*e*	0.8196(2)	0.4472(2)	0.4355(1)	0.112(1)	0.043(1)	0.067(1)	–0.0023(9)	0.045(1)	–0.0115(8)
O(4)	4*e*	0.8850(2)	0.6794(2)	0.39471(9)	0.092(1)	0.056(1)	0.0519(8)	–0.0048(8)	0.0373(8)	0.0059(7)
C(1)	4*e*	0.5075(3)	0.4689(2)	0.7297(1)	0.048(1)	0.049(1)	0.041(1)	0.002(1)	0.0091(9)	–0.002(1)
C(2)	4*e*	0.5863(2)	0.5832(2)	0.6675(1)	0.044(1)	0.043(1)	0.036(1)	0.0001(9)	0.0121(9)	–0.0009(9)
C(3)	4*e*	0.6654(2)	0.5386(2)	0.5874(1)	0.048(1)	0.040(1)	0.039(1)	–0.0018(9)	0.0102(9)	–0.0022(9)
C(4)	4*e*	0.7344(2)	0.6486(2)	0.5287(1)	0.044(1)	0.043(1)	0.034(1)	0.0012(9)	0.0126(8)	–0.0017(8)
C(5)	4*e*	0.7236(2)	0.8097(2)	0.5463(1)	0.042(1)	0.040(1)	0.041(1)	–0.0002(9)	0.0073(9)	–0.0003(9)
C(6)	4*e*	0.6449(3)	0.8506(2)	0.6307(1)	0.056(1)	0.041(1)	0.048(1)	0.002(1)	0.014(1)	–0.0055(9)
C(7)	4*e*	0.5799(3)	0.7417(2)	0.6882(1)	0.055(1)	0.052(1)	0.040(1)	0.003(1)	0.0166(9)	–0.005(1)
C(8)	4*e*	0.4347(3)	0.2067(2)	0.7544(2)	0.075(2)	0.050(1)	0.063(1)	–0.010(1)	0.022(1)	0.012(1)
C(9)	4*e*	0.7642(3)	1.0875(2)	0.5078(2)	0.072(2)	0.040(1)	0.067(1)	–0.001(1)	0.014(1)	0.004(1)

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