Crystal structure of (*E*)-4-methoxy-nitrophenone *N*-(2,4-dinitrophenyl)hydrazone, $C_{14}H_{11}N_5O_7$

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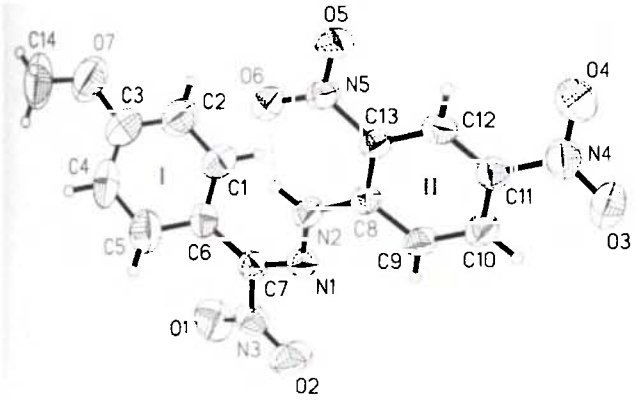

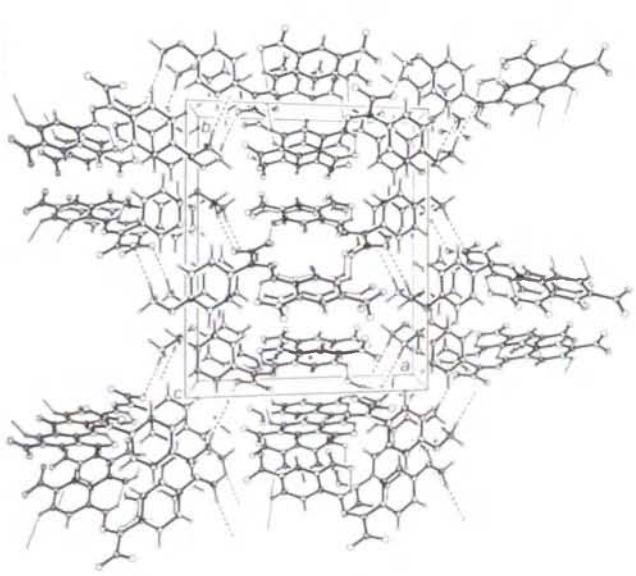

Abstract

$C_{14}H_{11}N_5O_7$, monoclinic, $P12_1/c1$ (no. 14), a = 15.075(2) Å, b = 17.683(3) Å, c = 6.099(1) Å, β = 100.43(1)°, V = 1599.0 Å^3, Z = 4, $R_{gt}(F)$ = 0.055, $wR_{ref}(F^2)$ = 0.175, T = 296 K.

Source of material

Reagents and solvents used were of commercially available quality. (*E*)-4-methoxybenzoyl-2-(2,4-dinitrophenyl)hydrazine (0.5 mmol, 158 mg) was dissolved in 100 mL dry CH_2Cl_2. Nitric oxide (NO) was produced by the reaction of 1 M H_2SO_4 solution with saturated $NaNO_2$ aqueous solution. The former was slowly added to the latter solution with stirring under argon atmosphere. NO was carried by argon and purified by passing it through a series of scrubbing bottles containing 4 M NaOH solution, distilled water and $CaCl_2$ in sequence. All of the bottles had been kept under argon atmosphere. The purified NO was bubbled through a previously degassed stirred stock solution at room temperature for an appropriate time. After completion of the reaction, as indicated by TLC, the reaction mixture was dried with anhydrous $MgSO_4$, concentrated in vacuo and purified by column chromatography on silica gel (200-300 mesh, ethyl acetate/hexane), then recrystallized from ethyl acetate/hexane (6:1, *v*/*v*), giving the title compound as straw-yellow needles (yield 95 %, m.p. 116 °C). Elemental analysis: found – C, 46.41 %; H, 3.11 %; N, 19.42 %; calc. for $C_{14}H_{11}N_5O_7$ – C, 46.50 %; H, 3.04 %; N, 19.38 %.

Discussion

Nitric oxide is a key signaling molecule in many biological processes, making regulation of nitric oxide levels highly desirable for human medicine and for advancing our understanding of basic physiology. Recent years have seen dramatic growth in our understanding of the biological role of nitric oxide NO. Therefore, the intensive research has been directed towards reactions of NO with biological molecules [1,2] or the anti-inflammatory drugs [3]. The number of publications concerning the reactivity of NO with various organic compounds has been grown rapidly [4-6]. Arylhydrazones have long been utilized for analysis of carbonyl compounds. In recent years, some of them and their complexes were found to have anti-cancer properties. In particular, hydrazones have been used to build chiral configurations and certain specific skeletons [7,8].

The crystal structure of the title compound is built up by only the $C_{14}H_{11}N_5O_7$ molecules (figure, top), in which all bond lengths are in normal ranges. The bond lengths of N2—C8, N4—C11, N5—C13 and N3—C7 are 1.368(4) A, 1.462(4) Å, 1.452(4) Å and 1.489(4) Å, respectively. It is obviously that the N2—C8 bond is much shorter than the other three bonds, which is due to the conjugation with the C8/C9/C10/C11/C12/C13 phenyl ring (ring II). The C7=N1 bond length of 1.272 Å is much shorter than the conventional double C=N bond length (1.34 Å – 1.38 Å), indicating that the C7=N1 is conjugated with the N2 atom. The analytical results show that the planes through ring II, the two attached nitro groups and the C7=N1–N2 unit are nearly parallel to each other, while the dihedral angles between the six-membered C1/C2/C3/C4/C5/C6 phenyl ring (ring I) and the C7=N1–N2 group is 61.8°. The respective torsion angles are ∠C7–N1–N2–C8 = –172.9(3)°, ∠N1–N2–C8–C13 = 179.8(3)°, ∠C1–C6–C7–N1 = 57.2(5)°. In the molecule, there is an intramolecular N–H···O hydrogen bond involving nitro O6 atom and hydrazone N2 atom. The crystal packing (figure, bottom) is characterized by alternate stacking of chains formed by weak C–H···O interactions (d(H···O) = 2.55 Å, 2.58 Å) and running along [100] direction.

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Table 1. Data collection and handling.

Crystal:	straw-yellow needle, size 0.12 × 0.34 × 0.58 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	1.23 cm^{-1}
Diffractometer, scan mode:	Siemens P4, ω
$2\theta_{max}$:	50.5°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	3199, 2898
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 1578
$N(param)_{refined}$:	237
Program:	SHELXTL [9]

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

Atom	Site	x	y	z	U_{iso}
H(2N)	4e	0.6876	0.6073	0.5324	0.053
H(1)	4e	0.7719	0.6929	0.8431	0.083
H(2)	4e	0.8937	0.7516	0.7451	0.095
H(4)	4e	1.0102	0.5543	0.6908	0.101
H(5)	4e	0.8854	0.4905	0.8026	0.094
H(9)	4e	0.4863	0.5682	0.6988	0.054
H(10)	4e	0.3448	0.5963	0.5106	0.058
H(12)	4e	0.4485	0.6919	0.0191	0.052
H(14A)	4e	1.1133	0.6175	0.6483	0.143
H(14B)	4e	1.1476	0.6950	0.5707	0.143
H(14C)	4e	1.0756	0.6481	0.4083	0.143

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)	4e	0.6516(2)	0.5590(1)	0.7858(4)	0.049(2)	0.040(1)	0.042(2)	0.001(1)	0.012(1)	0.003(1)
N(2)	4e	0.6410(2)	0.5950(1)	0.5877(4)	0.040(2)	0.051(2)	0.044(2)	−0.002(1)	0.013(1)	0.006(1)
N(3)	4e	0.7369(2)	0.5105(2)	1.1035(5)	0.071(2)	0.054(2)	0.044(2)	0.011(2)	0.009(2)	0.007(1)
N(4)	4e	0.2938(2)	0.6647(2)	0.1269(6)	0.049(2)	0.061(2)	0.066(2)	0.004(2)	0.007(2)	−0.000(2)
N(5)	4e	0.6162(2)	0.6743(1)	0.1606(5)	0.054(2)	0.034(1)	0.051(2)	0.001(1)	0.024(1)	0.001(1)
O(1)	4e	0.8097(2)	0.5099(2)	1.2276(5)	0.084(2)	0.118(3)	0.068(2)	0.019(2)	−0.005(2)	0.032(2)
O(2)	4e	0.6694(2)	0.4803(2)	1.1440(4)	0.089(2)	0.083(2)	0.068(2)	−0.012(2)	0.025(2)	0.026(2)
O(3)	4e	0.2299(2)	0.6343(2)	0.1875(5)	0.044(2)	0.095(2)	0.091(2)	−0.005(2)	0.012(1)	0.011(2)
O(4)	4e	0.2866(2)	0.7074(2)	−0.0319(5)	0.065(2)	0.101(2)	0.088(2)	0.007(2)	−0.004(2)	0.037(2)
O(5)	4e	0.5984(2)	0.7059(1)	−0.0203(4)	0.072(2)	0.063(2)	0.060(2)	0.012(1)	0.030(1)	0.026(1)
O(6)	4e	0.6950(2)	0.6630(1)	0.2551(4)	0.045(1)	0.061(2)	0.058(2)	−0.001(1)	0.018(1)	0.008(1)
O(7)	4e	1.0301(2)	0.6980(2)	0.6389(6)	0.082(2)	0.115(3)	0.126(3)	−0.015(2)	0.042(2)	−0.002(2)
C(1)	4e	0.8198(3)	0.6637(2)	0.8145(7)	0.058(2)	0.068(3)	0.084(3)	−0.011(2)	0.018(2)	0.003(2)
C(2)	4e	0.8919(3)	0.6991(3)	0.7531(7)	0.073(3)	0.079(3)	0.090(3)	−0.010(2)	0.025(3)	0.001(2)
C(3)	4e	0.9597(3)	0.6580(3)	0.7048(7)	0.073(3)	0.075(3)	0.072(3)	−0.014(2)	0.018(2)	−0.004(2)
C(4)	4e	0.9613(3)	0.5816(3)	0.7222(7)	0.048(2)	0.126(4)	0.082(3)	0.019(2)	0.021(2)	−0.009(3)
C(5)	4e	0.8859(3)	0.5429(3)	0.7902(7)	0.067(3)	0.081(3)	0.088(3)	0.007(2)	0.021(2)	−0.013(2)
C(6)	4e	0.8154(2)	0.5852(2)	0.8358(5)	0.042(2)	0.059(2)	0.046(2)	0.004(2)	0.008(2)	−0.001(2)
C(7)	4e	0.7323(2)	0.5526(2)	0.8902(5)	0.047(2)	0.041(2)	0.044(2)	0.005(2)	0.011(2)	0.002(2)
C(8)	4e	0.5564(2)	0.6118(2)	0.4747(5)	0.043(2)	0.035(2)	0.041(2)	−0.004(1)	0.011(1)	−0.001(1)
C(9)	4e	0.4795(2)	0.5929(2)	0.5621(5)	0.048(2)	0.047(2)	0.041(2)	−0.006(2)	0.011(2)	0.007(2)
C(10)	4e	0.3950(2)	0.6098(2)	0.4506(6)	0.046(2)	0.051(2)	0.051(2)	−0.005(2)	0.019(2)	0.001(2)
C(11)	4e	0.3842(2)	0.6471(2)	0.2485(5)	0.043(2)	0.040(2)	0.049(2)	−0.001(1)	0.006(2)	−0.002(2)
C(12)	4e	0.4567(2)	0.6670(2)	0.1556(5)	0.055(2)	0.034(2)	0.042(2)	0.001(2)	0.012(2)	0.003(1)
C(13)	4e	0.5427(2)	0.6496(2)	0.2677(5)	0.044(2)	0.035(2)	0.041(2)	−0.003(1)	0.015(1)	−0.002(1)
C(14)	4e	1.0964(3)	0.6621(3)	0.561(1)	0.064(3)	0.158(5)	0.140(5)	0.023(3)	0.035(3)	0.003(4)

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