The Crystal Structure of
2-Nitro-N-(4-nitrophenyl)benzamide

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2-Nitro-N-(4-nitrophenyl)benzamide was synthesized and characterized by spectroscopy and elemental analysis. The crystal structure was determined from single-crystal X-ray diffraction data. It crystallizes in the orthorhombic space group, P $2_12_12_1$, with unit cell dimensions a = 8.9443(10) Å, b = 9.7147(11) Å, and c = 13.8016(16) Å. The dihedral angle between the 2 aromatic rings is 82.32(4)°. The N2 and N3 nitro groups are oriented with respect to their attached phenyl rings at dihedral angles of 1.97(3)° and 15.73(3)°, respectively. The intramolecular C-H...O hydrogen bond results in the formation of a non-planar 6-membered ring. In the crystal structure, intermolecular N-H...O hydrogen bonds seem to be effective in the stabilization of the structure, resulting in the formation of a 3-dimensional network.

Key Words: X-ray structure, 2-nitro-N-(4-nitrophenyl)benzamide.

Introduction

The benzanilide core is present in compounds with such wide ranging biological activity that it has been called a privileged structure. Benzanilides serve as intermediates towards benzothiadiazin-4-ones,[1] quinazoline-2,4-diones,[2] benzodiazepine-2,5-diones,[3] and 2,3-disubstituted 3*H*-quinazoline-4-ones.[4] Benzanilides have established their efficacy as centroid elements of ligands that bind to a wide variety of receptor types. Thus, benzanilides containing amino alkyl groups, originally designed as a peptidomimetic, have been incorporated in an Arg-Gly-Asp cyclic peptide, yielding a high affinity GPIIb/IIIa ligand.[5] Imatinib, a drug used to treat some types of cancer, belongs to a new class of agents that act by inhibiting particular tyrosine kinase enzymes instead of non-specifically inhibiting rapidly dividing cells.[6] Pyridylmethyl-containing benzanilides are vascular endothelial growth factor receptor and tyrosine kinase inhibitors.[7] Furthermore, benzamides are

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reported to act as acetyl-CoA carboxylase and farnesyl transferase inhibitors.[8] We became interested in the synthesis of 2-nitro-N-arylbenzamide as an intermediates towards some new novel heterocycles and for the systematic study of their bioactive complexes. Herein we report the spectroscopic and crystal structure of the title compound (**1**) using single-crystal X-ray diffraction.

Experimental

Melting points were recorded using an MEL TEMP MP-D apparatus and are uncorrected. The ^{1}H-NMR and ^{13}C-NMR spectra were determined as solutions at 300 MHz (Bruker AM-400) and 100 MHz, respectively. FT IR spectra were recorded on an FTS 3000 MX spectrophotometer.

Synthesis of 1

A solution of 4-nitrobenzoyl chloride (1.75 g, 10 mmol) in dry THF (25 mL) was added dropwise to a solution of 4-nitro aniline (1.28 g, 10 mmol) in dry THF (15 mL) under a nitrogen atmosphere at reflux for 3 h. The reaction mixture was poured into 5 times its volume of cold water when the benzamide precipitated as a solid. Recrystallized from ethanol to afford **1** as colorless crystals (yield: 2.67 g; 88%; mp: 152 °C). IR (KBr) cm^{-1} 3251 (NH), 1667(CO), 1610 (arom.), 1529 1325, 1160, 744, 762; ^{1}H-NMR δ: 7.31 (2H, d, $J = 8.0$ Hz), 7.34 (2H, d, $J = 8.7$ Hz) 7.65 (2H, d, $J = 6.9$ Hz), 7.75 (2H, d, $J = 8.2$ Hz), 9.04 (1H, s, broad, NH); ^{13}C-NMR δ 165.4 (C = O),147.8, 134.6, 134.4, 132.7, 132.1, 130.3, 129.9, 129.3, 125.0. EIMS (m/z). 287 (M$^+$), 150 (100%). *Anal.* Calcd. For $C_{13}H_9N_3O_5$, C, 54.36; H, 3.16; N, 14.63 found C, 54.14; H, 3.51; N, 14.84.

X-Ray Data Collection and Structure Refinement

Experimental data are listed in Table 1. The atomic coordinates and equivalent isotropic displacement parameters for non-hydrogen atoms are reported in Table 2. The selected bond lengths and angles, and hydrogen-bond geometry are given in Tables 3 and 4, respectively. Crystallographic data were recorded on a Bruker-AXS SMART APEX CCD[9] diffractometer using Mo K$_\alpha$ radiation ($\lambda = 0.71073$ Å) at T = 120 K. Absorption correction was applied. The structure was solved by direct methods[9] and refined by full-matrix least-squares against F^2, using all data.[9] All non-H atoms were refined anisotropically. H atoms were positioned geometrically at distances of 0.88 Å (NH) and 0.95 Å (CH) from the parent C and N atoms; a riding model was used during the refinement process and the U$_{iso}$(H) values were constrained to be 1.2U$_{eq}$ (carrier atom).

Results and Discussion

Synthesis of **1** was carried out by slight modification of a published procedure.[4] Accordingly, 4-nitrobenzoyl chloride was treated with an equimolar amount of 4-nitro aniline in dry THF. The IR spectrum showed stretching vibrations at 3251 cm^{-1} for NH and at 1667 cm^{-1} for carbonyl. In the ^{1}H-NMR spectra the multiplet for aromatic protons at δ 7.31-7.75 and the characteristic broad singlet at δ 9.04 for NH were observed. ^{13}C-NMR showed peaks at δ 165.3 for C=O. Mass spectrum of the compound showed that the molecular ion peaks at m/z 287 and the base peak at m/z 150 originated from the aroyl cation. The

X-ray structural determination of the title compound **(1)** confirmed the assignment of its structure from spectroscopic data. The molecular structure of the title compound **(1),** along with the atom-numbering scheme, is depicted in Figure 1.

Table 1. Experimental Data.

Empirical formula	$C_{13} H_9 N_3 O_5$
Formula weight	287.23
Temperature	120(2) K
Wavelength (Mo K_α)	0.71073 Å
Crystal system	Orthorhombic
Space group	$P\ 2_1\ 2_1\ 2_1$
Unit cell dimensions	a = 8.9443(10) Å
	b = 9.7147(11) Å
	c = 13.8016(16) Å
Volume	1199.2(2) Å^3
Z	4
Density (calculated)	1.591 Mg/m^3
Absorption coefficient	0.126 mm^{-1}
F(000)	592
Crystal size	$0.30 \times 0.24 \times 0.14$ mm^3
Theta range for data collection (°)	2.56 to 27.88
Index ranges	$-11 \leq h \leq 10;\ -12 \leq k \leq 12;\ -18 \leq l \leq 17$
Reflections collected	10663
Independent reflections	1659 [$R_{int} = 0.0303$]
Completeness to theta = 27.88°	100.0%
Absorption correction Semi-empirical from equivalents	
Max. and min. transmission	0.9826 and 0.9633
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	1659/0/190
Goodness-of-fit on F^2	1.054
Final R indices [I > 2s (I)]	$R_1 = 0.0320$; $wR_2 = 0.0833$
R indices (all data)	$R_1 = 0.0352$; $wR_2 = 0.0853$
Largest diff. peak and hole	0.293 and -0.208 e.Å^{-3}

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{Å}^2 \times 10^3$).

Atom	x	y	z	U_{eq}
O1	−1227(2)r8159(1)	5458(1)	23(1)	
O2	881(2)	7543(2)	10252(1)	34(1)
O3	2619(2)	6015(2)	10082(1)	35(1)
O4	−2156(2)	5283(2)	5379(1)	30(1)
O5	−3563(2)	4650(2)	4191(1)	42(1)
N1	819(2)	6789(2)	5720(1)	19(1)
N2	1672(2)	6796(2)	9749(1)	25(1)
N3	−2452(2)	5213(2)	4514(1)	24(1)
C1	1000(2)	6863(2)	6733(1)	17(1)
C2	150(2)	7726(2)	7325(1)	21(1)
C3	382(2)	7706(2)	8321(1)	21(1)
C4	1459(2)	6840(2)	8699(1)	20(1)
C5	2326(2)	5995(2)	8122(1)	21(1)
C6	2093(2)	6010(2)	7134(1)	21(1)
C7	−322(2)	7316(2)	5182(1)	18(1)
C8	−345(2)	6790(2)	4151(1)	17(1)
C9	636(2)	7342(2)	3477(1)	20(1)
C10	539(2)	6977(2)	2507(1)	22(1)
C11	−548(2)	6065(2)	2194(1)	23(1)
C12	−1536(2)	5494(2)	2854(1)	22(1)
C13	−1408(2)	5852(2)	3824(1)	19(1)

U_{eq} is one-third of the trace of the orthogonalized U_{ij} tensor.

Table 3. Selected bond lengths (Å) and angles (°).

O1-C7	1.213(2)	N1-C7	1.361(2)
O2-N2	1.229(2)	N1-C1	1.409(2)
O3-N2	1.225(2)	N2-C4	1.463(2)
O4-N3	1.224(2)	N3-C13	1.471(2)
O5-N3	1.218(2)		
C7-N1-C1	127.45(15)	O5-N3-C13	118.00(16)
O3-N2-O2	123.48(16)	O4-N3-C13	118.07(16)
O3-N2-C4	118.67(17)	C2-C1-C6	120.38(16)
O2-N2-C4	117.85(16)	C2-C1-N1	123.27(16)
O5-N3-O4	123.93(17)	C6-C1-N1	116.35(16)

Table 4. Hydrogen bond geometry (Å and °).

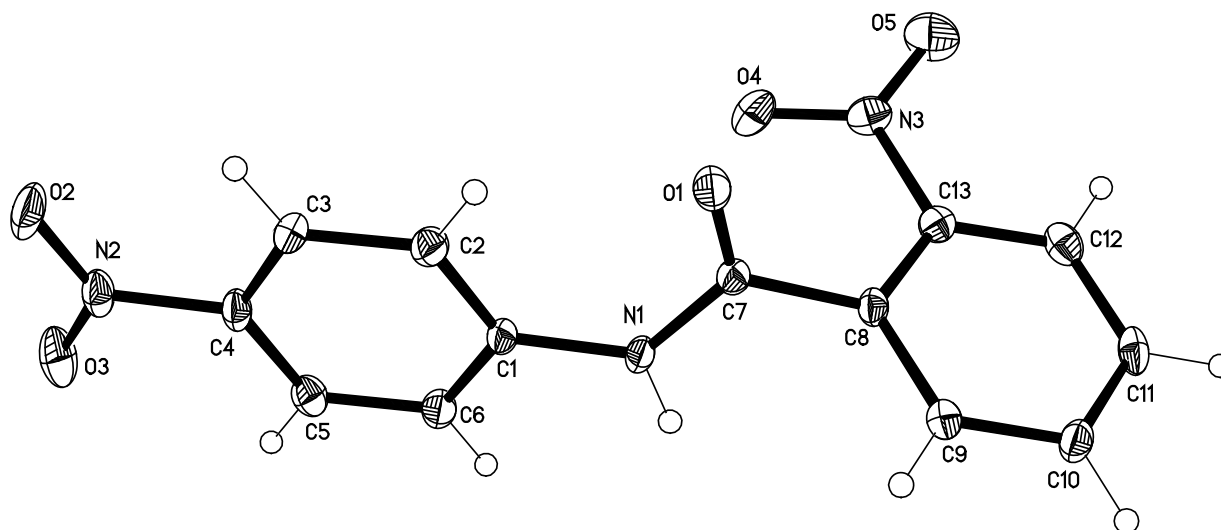| D-H $\cdots$ A	D-H	H $\cdots$ A	D $\cdots$ A	D-H $\cdots$ A
C2-H2A $\cdots$ O1	0.93	2.40	2.801(7)	106
N-H1A $\cdots$ O1^{i}	0.93	2.40	2.810(7)	106
N1-H1A $\cdots$ O3^{ii}	0.93	2.59	3.519(11)	173
Symmetry codes: (i) x +1/2; 3/2 - y; 1 - z ; (ii) 1/2 - x; 1- y; z − 1/2.				

Figure 1. The molecular structure of the title molecule with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.
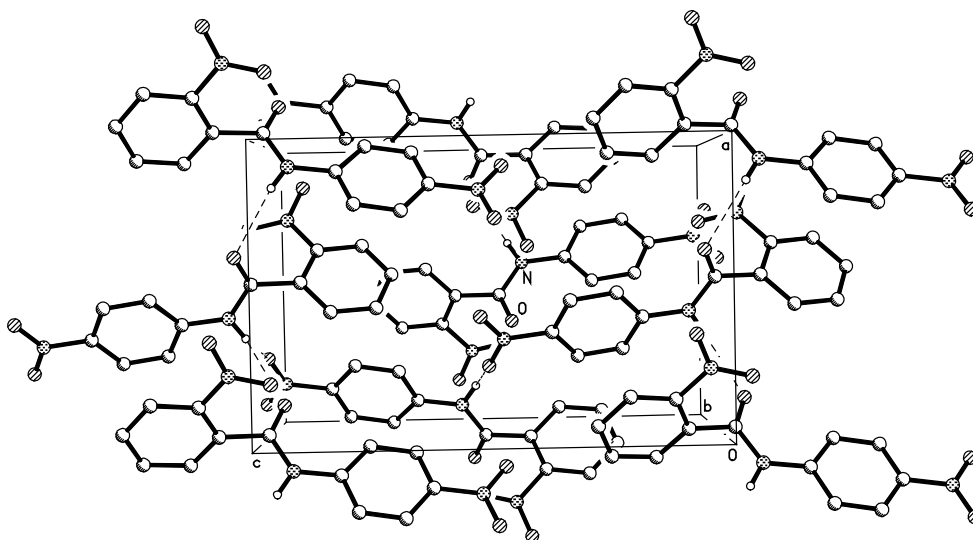

Figure 2. A packing diagram of **1**. Hydrogen bonds are shown as dashed lines. H atoms not involved in hydrogen bonding have been omitted for clarity.

Geometric parameters of the title compound **(1)** are in the usual ranges. The dihedral angle between the 2 aromatic rings is 82.32(4)°. The N2 and N3 nitro groups are oriented with respect to their attached

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phenyl rings at dihedral angles of 1.97(3)° and 15.73(3)°, respectively. The intramolecular C-H...O hydrogen bond (Table 4) results in the formation of a non-planar 6-membered ring. In the crystal structure, intermolecular N-H...O hydrogen bonds (Table 4) seem to be effective in the stabilization of the structure, resulting in the formation of a 3-dimensional network.

Supplementary Material

Crystallographic data for the structure reported in this paper have been deposited at the Cambridge Crystallographic Data Centre. Copies of the data (CCDC677249) can be obtained free of charge upon application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [e-mail: deposit@ccdc.cam.ac.uk].

Acknowledgements

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