

## Synthesis and Crystal Structure of Ethyl 4-(4-Nitrobenzamido)-3-(N-methyl-4-nitrobenzamido)-benzoate Monohydrate

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In this article, ethyl 4-(4-Nitrobenzamido)-3-(N-methyl-4-nitrobenzamido)benzoate monohydrate was synthesized through the reaction of 4-nitrobenzoyl chloride and 3,4-diamino benzoate using  $\text{Et}_3\text{N}$  as acid acceptor. The structure of the present compound was characterized using elemental analysis, IR,  $^1\text{H}$  NMR spectra and X-ray crystallography. The compound crystallizes in the triclinic system, space group P-1, with cell dimensions of  $a = 7.394(6)$ ,  $b = 11.418(8)$ ,  $c = 14.293(11)\text{\AA}$ ,  $\alpha = 84.132(13)$ ,  $\beta = 81.034(13)$ ,  $\gamma = 89.451(13)^\circ$ ,  $V = 1185.7(16)\text{\AA}^3$  and  $Z = 2$ .

**Key Words:** 4-(4-Nitrobenzamido)-3-(N-methyl-4-nitrobenzamido)benzoate monohydrate, Crystal structure, Synthesis.

### INTRODUCTION

Aramid fibers such as Kevlar and poly(*p*-benzamide) are known to be one of the most tough organic fabrication materials and have been used as a content of bulletproof jackets. The aramide block copolymers<sup>1,2</sup> are expected to be arranged to form intriguing nanostructures by virtue of multiple hydrogen bondings between the same length polymers. A soluble block copolymer containing poly(*p*-benzamide) was synthesized not only because of deprotection of poly(N-octyl-*p*-benzamide) unit. It can be identified directly by analysis of the block copolymer as well as the strong intermolecular forces of well-defined poly(*p*-benzamide) must have the block copolymer self-assemble in an unprecedented manner<sup>3</sup>. Aromatic polyamides form a relevant family of polymers which attracts interest of many research groups, at both the academic and industrial levels, not only as high performance materials but also for their peculiar conformational and physicochemical behaviours. The presence of both aromatic and amide groups, differently linked and oriented along the chain, allows for the preparation of a wide variety of aramide structures, ranging from flexible to rigid ones<sup>4,6</sup>. In recent years it has been suggested<sup>7-9</sup> that N-allylation of aromatic amide groups strongly decreases the stiffness of the polyamide

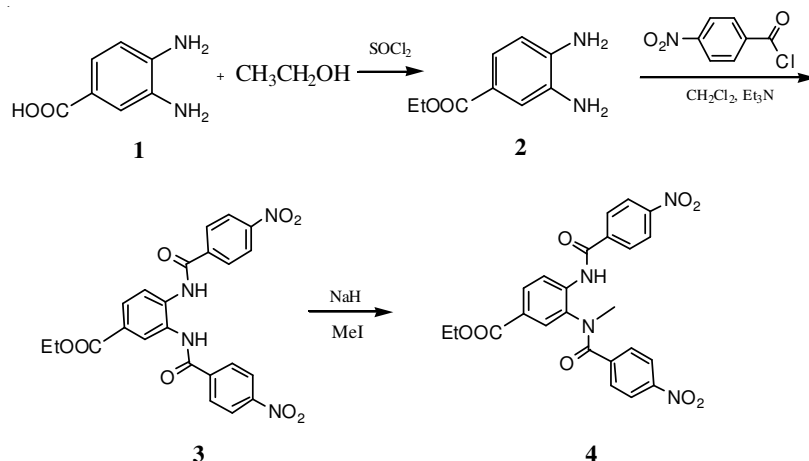
chain, increasing at the same time its solubility in common organic solvents, owing to its capability of destroying hydrogen bonding. In our ongoing studies of the structure of amide-type acyclic polyether with 1,3-dihydroxybenzene as a skeleton, ethyl 4-(4-Nitrobenzamido)-3-(N-methyl-4-nitrobenzamido)benzoate monohydrate was obtained.

## EXPERIMENTAL

All the reagents were obtained commercially and used without further purification. Elemental analysis was performed by Perkin-Elmer 240 analyzer. Infrared (IR) spectra were recorded on a Nicolet 510P FT-IR spectrophotometer with KBr tablets.  $^1\text{H}$  NMR spectra were recorded on a Rigaku JNM-ECP 600 spectrometer using DMSO- $d_6$  as solvent and TMS as internal standard.

**Preparation of the title compound:** A solution of 4-nitrobenzoyl chloride (5.55 g, 30 mmol) in  $\text{CH}_2\text{Cl}_2$  (40 mL) was added dropwise over a period of 2 h to a solution of ethyl 3,4-diaminobenzoate (5.40 g, 30 mmol) and  $\text{Et}_3\text{N}$  (8.3 mL) in  $\text{CH}_2\text{Cl}_2$  (50 mL). After the addition was completed, the reaction mixture was stirred at 273 K for 1 h and at room temperature for 3 h. The volatiles were removed *in vacuo* to give an off-white solid as **3**. To a solution of **3** (8.60 g, 18 mmol) in THF (50 mL) was slowly added NaH (60 % w/w dispersion in mineral oil, 0.78 g, 20 mmol) at  $0^\circ\text{C}$ . After 0.5 h, the reaction mixture was warmed to room temperature and stirred for an additional 40 min and quenched with MeI (2.8 mL, 45 mmol). After 13 h at room temperature, the volatiles were removed *in vacuo* and the residue was partitioned between  $\text{CH}_2\text{Cl}_2$  and water. Single crystals were obtained by slow evaporation of a glacial AcOH solution at room temperature over a period of 1 week. (%) Analysis: Calcd. for  $\text{C}_{24}\text{H}_{20}\text{N}_4\text{O}_8\cdot\text{H}_2\text{O}$ : C, 55.65, H, 4.06, N, 11.29; Found: C 55.86, H 3.95, N 11.48. IR data ( $\text{cm}^{-1}$ ): 3462m, 3111m, 2924m, 2852m, 1715s, 1688s, 1648s, 1250s, 1106s, 851m, 720s.  $^2\text{H}$  NMR (400 MHz, DMSO): 1.34 (t, 3H), 2.48 (s, 3H), 4.49 (tetra, 2H), 7.80 (m, 2H), 7.90 (s, 1H), 8.18 (m, 4H), 8.40 (m, 5H). The scheme of isolation of the title complex was shown in **Scheme-I**.

**Crystallographic study:** A suitable crystal of the title compound was mounted on a Siemens SMART 1000 CCD area-detector diffractometer. Reflection data were measured at  $20^\circ\text{C}$  under  $\text{MoK}_\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ) with a graphite monochromator. Empirical absorption correction were carried out by using the SADABS<sup>10</sup> program. The structure of the present compound was solved by direct methods and refined by least squares on  $F^2$  by using the SHELXTL<sup>11</sup> software package. All non-H atoms were anisotropically refined. Atomic scattering factors and anomalous dispersion corrections were taken from International Tables for X-Ray crystallography<sup>12</sup>.



**Scheme-I** Synthetic route of ethyl 4-(4-Nitrobenzamido)-3-(N-methyl-4-nitrobenzamido)benzoate monohydrate

Crystal data and structure refinement for the title compound are shown in Table-1. Selected bond lengths and angles are presented in Table-2. The hydrogen-bonding interaction distances are listed in Table-3.

TABLE-1  
CRYSTAL DATA AND STRUCTURE REFINEMENT PARAMETERS  
FOR THE PRESENT COMPOUND

Formula	C <sub>24</sub> H <sub>20</sub> N <sub>4</sub> O <sub>8</sub> .H <sub>2</sub> O
Formula weight	826.86
Crystal system	Triclinic
Space group	P-1
a(Å)	7.394(6)
b(Å)	11.418(8)
c(Å)	14.293(11)
α(°)	84.132(13)
β(°)	81.034(13)
γ(°)	89.451(13)
Volume (Å <sup>3</sup> )	1185.7(16)
Z	2
D(calc) [g/cm <sup>3</sup> ]	1.430
F(000)	532
μ(MoKa) [mm <sup>-1</sup> ]	0.111
Crystal Size (mm <sup>3</sup> )	0.08 × 0.14 × 0.31
Temperature (K)	293
Wavelength (Å)	0.71073
θ range for data collection (°)	1.5-26.1
Dataset	-9 ≤ h ≤ 9 ; -10 ≤ k ≤ 14 ; -17 ≤ l ≤ 16
R, wR	0.0739, 0.1918
S	0.97

TABLE-2  
SELECTED BOND LENGTHS (Å) AND ANGLES (°) FOR THE  
PRESENT COMPOUND

O1-N1	1.222(6)	N1-C3	1.476(5)
O2-N1	1.209(6)	N2-C7	1.345(5)
O3-C7	1.234(5)	N2-C24	1.466(5)
O4-C14	1.208(5)	N2-C8	1.436(5)
O5-N4	1.205(6)	N3-C14	1.370(5)
O6-N4	1.214(7)	N3-C13	1.398(5)
O7-C21	1.190(7)	N4-C18	1.468(7)
O8-C21	1.324(7)	C22-C23A	1.35(6)
O8-C22	1.465(8)	C22-C23B	1.27(2)
O1-N1-O2	123.7(4)	O6-N4-C18	117.9(4)
O2-N1-C3	118.7(4)	O5-N4-C18	118.5(5)
O1-N1-C3	117.6(4)	O3-C7-C6	118.5(4)
C7-N2-C8	123.6(3)	N2-C7-C6	120.5(4)
C8-N2-C24	116.2(3)	O3-C7-N2	121.0(3)
C7-N2-C24	118.4(3)	N3-C14-C15	116.0(4)
C13-N3-C14	126.9(3)	O4-C14-C15	120.1(4)
O5-N4-O6	123.5(5)	O4-C14-N3	123.9(4)

TABLE-3  
HYDROGEN-BONDING GEOMETRY (Å, °)

D—H...A	D—H	H...A	D...A	D—H...A
N3—H3A...O1W <sup>i</sup>	0.86	2.16	2.925(6)	148
O1W—H1W1...O1 <sup>ii</sup>	0.84(6)	2.13(6)	2.949(6)	164(6)
O1W—H2W1...O3	0.92(6)	1.92(6)	2.814(6)	166(5)
C1—H1A...O7 <sup>iii</sup>	0.93	2.44	3.056(6)	124
C12—H12A...O4	0.93	2.21	2.821(6)	122
C22—H22D...O7	0.97	2.27	2.677(1)	104
C24—H24A...O3	0.96	2.27	2.688(5)	105

Symmetry Code: (i) -x, 1-y, 1-z; (ii) x, -1+y, z; (iii) -1+x, y, z

## RESULTS AND DISCUSSION

Fig. 1 shows the molecular structure of the compound. Packing diagram of the title compound in a unit cell is shown in Fig. 2. The compound crystallizes in the triclinic system, space group P-1, with cell dimensions of  $a = 7.394(6)$ ,  $b = 11.418(8)$ ,  $c = 14.293(11)$  Å,  $\alpha = 84.132(13)$ ,  $\beta = 81.034(13)$ ,  $\gamma = 89.451(13)^\circ$ ,  $V = 1185.7(16)$  Å<sup>3</sup> and  $Z = 2$ . In the nonplanar molecule, all bond lengths and angles are within normal range<sup>13</sup> and comparable to the corresponding values in the related structure<sup>14</sup>. The dihedral angles between the central benzene ring (C8-C13) and the two outer benzene rings (C1-C6 and C5-C20) are  $62.1(2)$  and  $37.4(2)^\circ$ , respectively, while

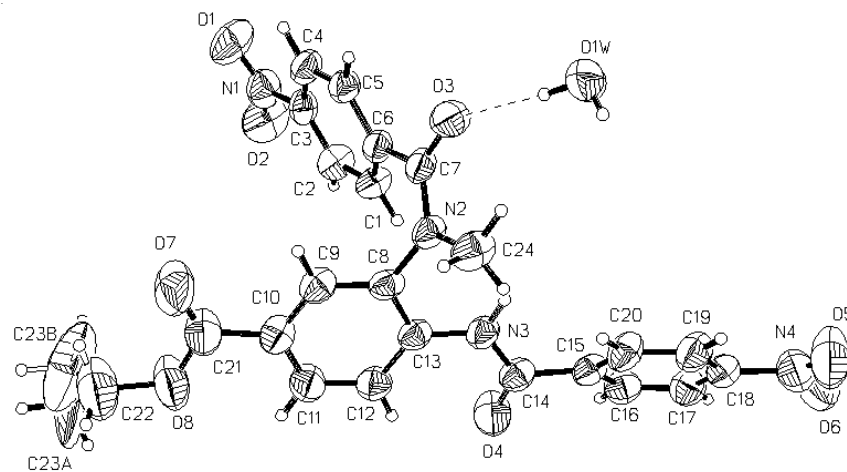


Fig. 1. Structure of the complex with the atomic numbering scheme, Displacement ellipsoids are shown at the 50% probability level

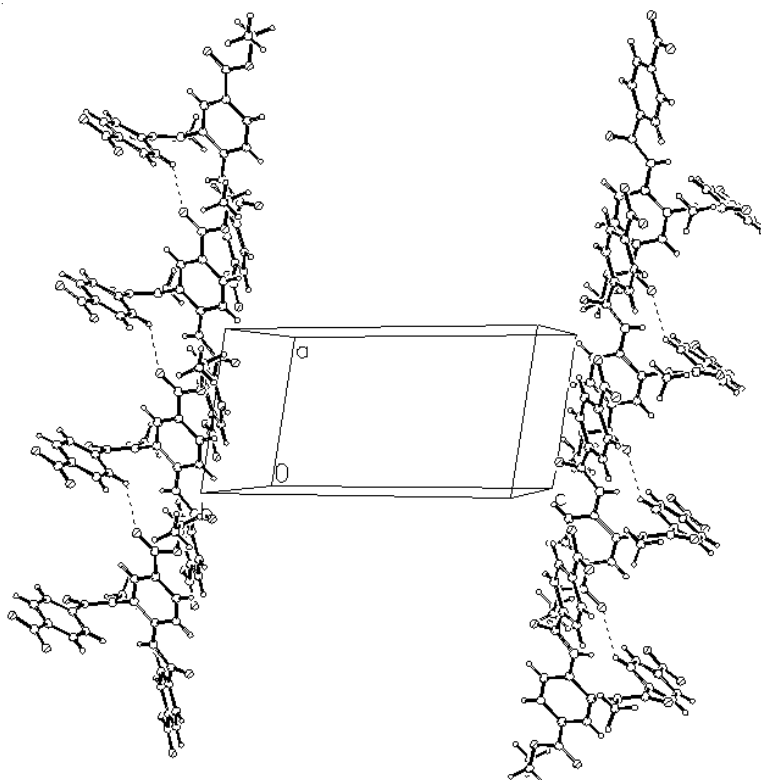


Fig. 2. View of the crystal packing for the present compound

the two outer benzene rings make a dihedral angle of 50.6(2)°. All the carbonyl O atoms are involved in intramolecular C—H...O interactions, forming five- and six-membered rings. The water molecule is linked to the molecule through intramolecular O1W—H2W1...O3 hydrogen bond. In the crystal structure, molecules are linked into chains along the a axis by C—H...O hydrogen bonds. The chains are connected into three-dimensional network by N3—H3A...O1W and O1W—H1W1...O1 interactions. The packing is further stabilized by  $\pi$ ... $\pi$  interactions between the C1-C6 benzene rings, the distance between the centroids, Cg...Cg<sup>iv</sup> and the interplanar distance are 3.899(2) and 3.395(2) Å, respectively [Symmetry code: (iv) 2-x, -y, 1-z]. The C23 atom shows positional disorders. Refinement of the site occupancies resulted in major and minor component with occupancies of 72 and 28 % for C23A and C23B, respectively.

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