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Synthesis and Structural Characterization of Propane-1,3-diamino *Bis*[3,4,5,6-tetrabromo-2-(methoxycarbonyl)benzoate] Water Monosolvate

ZU-PEI LIANG* and JIAN LI

Department of Chemistry and Chemical Engineering, Weifang University, Weifang 261061, P.R. China

*Corresponding author: Tel: +86 536 8877561; E-mail: zupeiliang@163.com

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The present compound propane-1,3-diamino *bis*[3,4,5,6-tetrabromo-2-(methoxycarbonyl)benzoate] water monosolvate ($C_{21}H_{22}Br_8N_2O_{10}$, M_r = 1101.69) was synthesized and characterized by single crystal X-ray diffraction. The crystal belongs to monoclinic, space group Pc, with a = 11.9484(13), b = 8.0805(9), c = 16.6897(18) Å, β = 103.5690(10)º, V = 1566.4(3) Å^3, Z = 2, D_c = 2.336 g/cm^3, λ = 0.71073 Å, μ(MoK$_\alpha$) = 10.294 mm^{-1}, $F_{(000)}$ = 1044. The final refinement gave R = 0.0475, wR(F^2) = 0.1001 for 4,887 observed reflections with I > 2σ(I). The asymmetric unit of the title compound contains one propane-1,3-diaminium cation, two 3,4,5,6-tetrabromo-2-(methoxycarbonyl)benzoate anions and two water molecules. In one of the anions, the mean planes of the methoxycarbonyl and carboxylate groups form dihedral angles of 55.0(3) and 70.7(3)º, respectively with the benzene ring. And in another one, the mean planes of the methoxycarbonyl and carboxylate groups form dihedral angles of 48.6(3) and 49.9(3)º, respectively with the benzene ring. In the crystal, intermolecular N-H···O, N-H···Br and C-H···O hydrogen bonds connect the components of the structure to form a three-dimensional network.

Key Words: Propane-1,3-diamino *bis*[3,4,5,6-tetrabromo-2-(methoxycarbonyl)benzoate], Monosolvate, Synthesis.

INTRODUCTION

N,N'-*Bis*(tetrabromphthalimide) predominant products have been found to be useful flame retardants in polyesters, *e.g.*, polybutylene terephthalate and other resin formulations[1]. 1,3-*Bis*(tetrabromophthalimidine)propane is one of them. 2-(Methoxycarbonyl)-3,4,5,6-tetrabromobenzoic acid is the intermediate of the N,N'-*bis*(tetrabromophthalimide). In the present work, the reaction of 3,4,5,6-tetrabromo-2-(methoxycarbonyl)benzoic acid and 1,3-diamino propane in methanol is expected to yield 1,3-*bis*(tetrabromophthalimidine)propane. However, the product is propane-1,3-diamino *bis*[3,4,5,6-tetrabromo-2-(methoxycarbonyl)benzoate] water monosolvate. In this paper, the synthesis and the crystal structure of the title compound is reported.

EXPERIMENTAL

Synthesis of propane-1,3-diamino *bis*[3,4,5,6-tetrabromo-2-(methoxycarbonyl)benzoate] water monosolvate compound: All the reagents were of AR grade and used without further purification. A mixture of 4,5,6,7-tetrabromoisobenzofuran-1,3-dione (4.64 g, 0.01 mol) and methanol (15 mL) was refluxed for 0.5 h. Then propane-1,3-diamine (0.37 g, 0.005 mol) was added to the above solution and mixed round for 20 min at room temperature, precipitate was found. And then 2 mL water was added, the above precipitate was dissolved. The solution was kept at room temperature for 8 d. Natural evaporation gave colourless single crystals of the title compound, suitable for X-ray analysis.

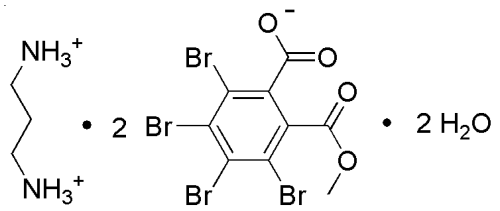
Data collection and structure determination: A selected crystal of the title compound was mounted on a SMART CCD diffractometer. The reflection data were measured at 298 K, using a graphite monochromator MoK$_\alpha$ (λ = 0.71073 Å) radiation with an ω-2θ scan mode. The total reflections were 7,715 with 4,887 independent ones (R_{int} = 0.0455), of which 374 were observed with I > 2σ(I). Intensities were corrected for Lorentz and polarization effects and empirical absorption and all data were corrected using SADABB[2] program.

The structure was solved by direct methods using SHELXS-97[3] program. All the non-hydrogen atoms were refined on F^2 anisotropically by full-matrix least squares method. All hydrogen atoms were placed in the geometrically calculated positions. The contributions of these hydrogen atoms were included in the structurefactor calculations. The atomic scattering factors and anomalous dispersion corrections were taken from International Table for X-ray crystallography[4]. The final least-square cycle gave R = 0.0475 and ωR = 0.1001 (w = 1/[σ^2(Fo^2) + (0.0454P^2 + 0.0000P], where P =

$(Fo^2 + 2Fc^2)/3)$. S = 1.008, $(\Delta\rho)_{min}$ = -0.495 and $(\Delta\rho)_{max}$ = 0.841 e/Å^3. CIF file containing complete information on the studied structure was deposited with CCDC, deposition number 824558 and is freely available upon request from the following web site: www.ccdc.cam.ac.uk/data_request/cif

RESULTS AND DISCUSSION

In the present work, the reaction of 3,4,5,6-tetrabromo-2-(methoxycarbonyl)benzoic acid and 1,3-diamino propane in methanol is expected to yield 1,3-*bis*(tetrabromophthalimidine)propane. However, the product is propane-1,3-diaminium *bis*[3,4,5,6-tetrabromo-2-(methoxy-carbonyl)-benzoate] water monosolvate (**Scheme-I**), this may be the reason of a short time and a cool temperature in the reaction.



Scheme-I: Chemical structural formula of the title compound

The selected bond distances and bond angles are listed in Table-1. A displacement ellipsoid plot with atomic numbering scheme is shown in Fig. 1 and a perspective view of the crystal packing in the unit cell is shown in Fig. 2. Hydrogen bond schemes (Å, º) are listed in Table-2.

TABLE-1
SELECTED BOND LENGTHS (Å) AND BOND ANGLES (º)

Bond	Length (Å)	Bond	Angle (º)
Br(1)-C(5)	1.910(14)	C(1)-O(1)-C(9)	114.6(12)
Br(2)-C(6)	1.897(14)	C(10)-O(5)-C(18)	114.3(12)
Br(3)-C(7)	1.852(14)	O(2)-C(1)-O(1)	126.4(15)
Br(4)-C(8)	1.879(13)	O(2)-C(1)-C(3)	124.4(14)
Br(5)-C(14)	1.900(12)	O(1)-C(1)-C(3)	109.0(13)
Br(6)-C(15)	1.868(14)	O(4)-C(2)-O(3)	124.5(17)
Br(7)-C(16)	1.875(14)	O(4)-C(2)-C(4)	118.4(15)
Br(8)-C(17)	1.881(13)	O(3)-C(2)-C(4)	117.0(14)
O(1)-C(1))	1.271(15)	C(3)-C(4)-C(2)	116.6(13)
O(1)-C(9)	1.469(17)	C(4)-C(3)-C(1)	121.3(13)
O(2)-C(1)	1.147(15)	O(6)-C(10)-O(5)	125.3(15)
O(3)-C(2)	1.211(17)	O(6)-C(10)-C(12)	121.9(13)
O(4)-C(2)	1.195(16)	O(5)-C(10)-C(12)	112.8(13)
O(5)-C(10)	1.307(16)	O(8)-C(11)-O(7)	121.6(15)
O(5)-C(18)	1.467(18)	O(8)-C(11)-C(13)	118.9(13)
O(6)-C(10)	1.184(15)	O(7)-C(11)-C(13)	119.1(12)
O(7)-C(11)	1.232(15)	C(17)-C(12)-C(10)	120.4(12)
O(8)-C(11)	1.162(14)	C(12)-C(13)-C(11)	116.2(13)

The asymmetric unit of the title compound contains one propane-1,3-diaminium cation, two 3,4,5,6-tetrabromo-2-(methoxycarbonyl)benzoate anions and two water molecules. In one of the anions, the mean planes of the methoxycarbonyl and carboxylate groups form dihedral angles of 55.0(3) and 70.7(3)º, respectively with the benzene ring. And in another one, the mean planes of the methoxycarbonyl and carboxylate groups form dihedral angles of 48.6(3) and 49.9(3)º,

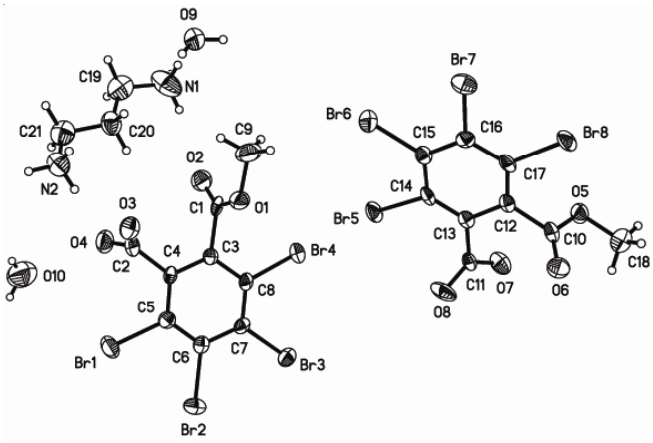


Fig. 1. Molecular structure with atomic numbering scheme

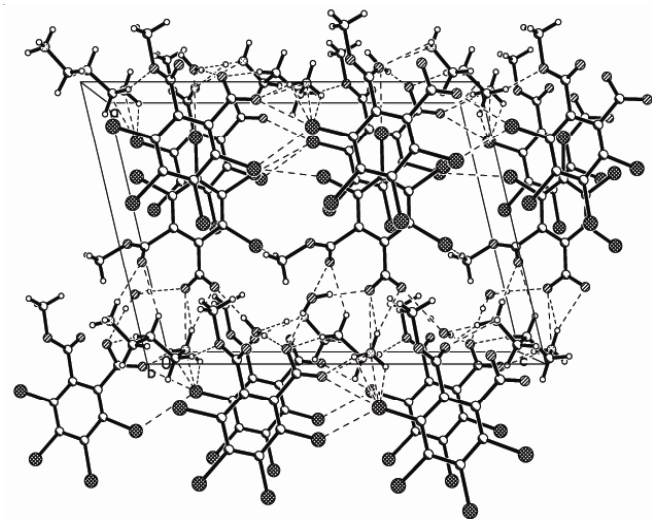


Fig. 2. View of crystal packing down the b-axis

TABLE-2
HYDROGEN BOND SCHEMES (Å, º)

D-H···A	D-H	H···A	D-A	D-H···A
N1-H1A…O9	0.89	1.98	2.83	157
N1-H1B…O6[a]	0.89	2.24	2.92	132
N1-H1B…O10[b]	0.89	2.13	2.65	116
N1-H1C…O2	0.89	2.58	3.26	134
N2-H2A…O3	0.89	2.01	2.81	149
N2-H2A…O4	0.89	2.44	3.24	150
N2-H2B…Br8[c]	0.89	2.81	3.35	121
N2-H2B…Br3[d]	0.89	3.15	3.94	150
N2-H2C…O8[d]	0.89	1.93	2.80	166
O9-H9F…O4[e]	0.85	1.89	2.73	171
O9-H9G…O7[d]	0.85	1.94	2.79	171
O10-H10C…O3[f]	0.85	2.04	2.88	173
O10-H10D…O7[g]	0.85	2.03	2.88	174

Symmetry codes: (a) -1+x, -1+y, z (b) x, -y, -1/2+z (c) -1+x, 2-y, 1/2+z (d) -1+x, y, z (e) x, 1-y, -1/2+z (f) x, 1-y, 1/2+z (g) 1+x, 1-y, 1/2+z

respectively with the benzene ring. The bond lengths and angles are in agreement with those in propan-1-amino-3,4,5,6-tetrabromo-2-(methoxycarbonyl)benzoate N,N-dimethyl-formamide monosolvate[5], 2-methylanilinium 3,4,5,6-tetra-bromo-2-(methoxy-carbonyl)benzoate methanol monosolvate[6] and in ethane-1,2-diamino *bis*[2-(methoxy-carbonyl)-3,4,5,6-tetrabromobenzoate] methanol solvate[7]. In crystal, intermolecular N-H···O, N-H···Br and C-H···O hydrogen bonds connect

the components of the structure to form a three-dimensional network (Fig. 2 and Table-2).

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