



NOTE

Synthesis and Crystal Structure of Aminium 2-(Carbonyl)-3,4,5,6-tetrabromobenzoate 3,4,5,6-Tetrabromobenzene-1,2-dioic Acid Propanone Monosolvate

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The compound aminium 2-(carbonyl)-3,4,5,6-tetrabromobenzoate 3,4,5,6-tetrabromobenzene-1,2-dioic acid propanone monosolvate ($C_{19}H_{13}Br_8NO_9$, $M_r = 1038.58$) was synthesized and characterized by single crystal X-ray diffraction. The crystal belongs to monoclinic, space group $C2/c$, with $a = 23.870(2)$, $b = 10.8790(10)$, $c = 12.2069(13)$ Å, $\beta = 107.186(2)^\circ$, $V = 3028.4(5)$ Å³, $Z = 4$, $D_c = 2.278$ g/cm³, $\lambda = 0.71073$ Å, $\mu(\text{MoK}\alpha) = 10.638$ mm⁻¹, $F_{(000)} = 1944$. The final refinement gave $R = 0.1176$, $wR(F^2) = 0.2719$ for 7,196 observed reflections with $I > 2\sigma(I)$. The asymmetric unit of the title compound contains one aminium cation, one 2-(carbonyl)-3,4,5,6-tetrabromobenzoate anion, one 3,4,5,6-tetrabromobenzene-1,2-dioic acid molecule and one propanone molecule. In the anions, the mean planes of the carbonyl and carboxylate groups form dihedral angles of $68.1(3)$ and $62.7(3)^\circ$, respectively with the benzene ring. In the crystal, intermolecular $N-H\cdots O$, $N-H\cdots Br$ and $O-H\cdots O$ hydrogen bonds connect the components of the structure to form a two-dimensional network.

Key Words: Aminium 2-(carbonyl)-3,4,5,6-tetrabromobenzoate, Monosolvate, Synthesis, Crystal structure.

Tetrabromophthalimide and its derivatives have been found to be useful flame retardants in polyesters, *e.g.*, polybutylene terephthalate and other resin formulations¹. Several intermediates of them have been synthesized in the previous work²⁻⁴. In present work, the reaction of tetrabromophthalic anhydride and amine in propanone is expected to form 4,5,6,7-tetrabromoisoindoline-1,3-dione, but instead formed aminium 2-(carbonyl)-3,4,5,6-tetrabromobenzoate 3,4,5,6-tetrabromobenzene-1,2-dioic acid propanone monosolvate. This may have happened because of the presence of water for the reaction. In this paper, the synthesis and the crystal structure of aminium 2-(carbonyl)-3,4,5,6-tetrabromobenzoate 3,4,5,6-tetrabromobenzene-1,2-dioic acid propanone monosolvate is reported.

Synthesis of the aminium 2-(carbonyl)-3,4,5,6-tetrabromobenzoate 3,4,5,6-tetrabromobenzene-1,2-dioic acid propanone monosolvate: All the reagents were of AR grade and used without further purification. A mixture of tetrabromophthalic anhydride (4.64 g, 0.01 mol) and ammonia water (25 %) (0.68 g, 0.01 mol) in propanone (15 mL) was refluxed for 0.5 h. And then the solution was kept at room temperature for 9 d. Natural evaporation gave colourless single crystals of aminium 2-(carbonyl)-3,4,5,6-tetrabromobenzoate 3,4,5,6-tetrabromobenzene-1,2-dioic acid propanone monosolvate, 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 $\text{MoK}\alpha$ ($\lambda = 0.71073$ Å) radiation with an ω - 2θ scan mode. The total reflections were 7,196 with 2,629 independent ones ($R_{\text{int}} = 0.2158$), of which 175 were observed with $I > 2\sigma(I)$. Intensities were corrected for Lorentz and polarization effects and empirical absorption and all data were corrected using SADABB⁵ program.

The structure was solved by direct methods using SHELXS-97⁶ 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 structure factor calculations. The atomic scattering factors and anomalous dispersion corrections were taken from International Table for X-ray crystallography⁷. The final least-square cycle gave $R = 0.1176$ and $wR = 0.2719$ ($w = 1/[\sigma^2(F_o^2) + (0.1592P)^2 + 0.0000P]$, where $P = (F_o^2 + 2F_c^2)/3$). $S = 1.061$, $(\Delta\rho)_{\text{min}} = -3.125$ and $(\Delta\rho)_{\text{max}} = 4.119$ e/Å³. CIF file containing complete information on the studied structure was deposited with CCDC, deposition number 824533 and is freely available upon request from the following web site: www.ccdc.cam.ac.uk/data_request/cif

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 mLeW of the crystal packing in the unit cell is shown in Fig. 2. Hydrogen bond schemes (\AA , $^\circ$) are listed in Table-2.

Bond	Length (\AA)	Bond	Angle ($^\circ$)
Br(1)-C(5)	1.85(2)	O(2)-C(1)-O(1)	124(2)
Br(2)-C(6)	1.91(2)	O(2)-C(1)-C(3)	115(2)
Br(3)-C(7)	1.89(2)	O(1)-C(1)-C(3)	120.5(18)
Br(4)-C(8)	1.89(2)	O(4)-C(2)-O(3)	126(2)
O(1)-C(1)	1.27(3)	O(4)-C(2)-C(4)	119(2)
O(2)-C(1)	1.26(2)	O(3)-C(2)-C(4)	115(2)
O(3)-C(2)	1.27(3)	C(8)-C(3)-C(1)	120(2)
O(4)-C(2)	1.20(3)	C(5)-C(4)-C(2)	116(2)
O(5)-C(9)	1.24(4)	C(4)-C(3)-C(1)	119.5(18)
—	—	C(3)-C(4)-C(2)	123(2)

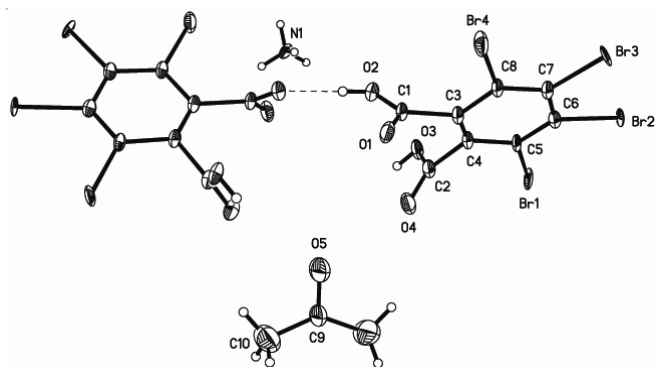


Fig. 1. Molecular structure with atomic numbering scheme

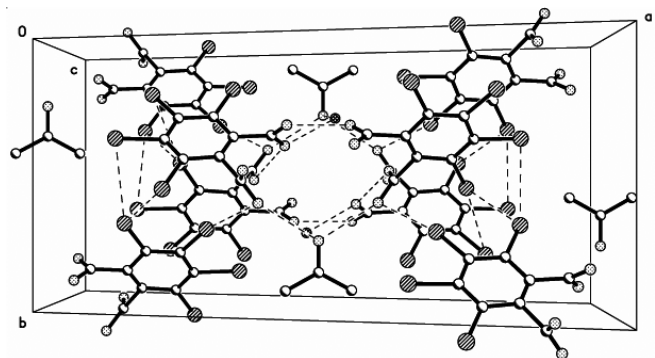


Fig. 2. View of crystal packing down the c-axis

D-H...A	D-H	H...A	D-A	D-H...A
N1-H1A...O1 ^a	0.90	1.86	2.76	176
N1-H1B...O5	0.90	1.93	2.83	172
N1-H1C...O3 ^b	0.90	2.33	3.19	161
N1-H1D...Br2	0.90	2.91	3.50	124
O2-H2...O2 ^c	0.82	1.69	2.50	171
O3-H3...O1 ^d	0.82	1.82	2.61	159

Symmetry codes: (a) $x, 1-y, -1/2+z$, (b) $1/2-x, 1/2-y, -z$ (c) $1-x, y, 1/2-z$ (d) $-1/2+x, 1/2-y, -1/2+z$.

The asymmetric unit of the title compound contains one aminium cation, one 2-(carbonyl)-3,4,5,6-tetrabromobenzoate anion, one 3,4,5,6-tetrabromobenzene-1,2-dioic acid molecule and one propanone molecule (Fig. 1). The bond lengths and angles are in agreement with those in propane-1,3-diaminium bis[3,4,5,6-tetrabromo-2-(methoxycarbonyl)benzoate] water monosolvate², cyclohexaninium 3,4,5,6-tetrachloro-2-(methoxycarbonyl)benzoate³ and ethylammonium 2-(methoxycarbonyl)-3,4,5,6-tetrabromobenzoate methanol solvate⁴. In the anions, the mean planes of the carbonyl and carboxylate groups form dihedral angles of $68.1(3)$ and $62.7(3)^\circ$, respectively with the benzene ring. In the crystal, intermolecular N-H...O, N-H...Br and O-H...O hydrogen bonds connect the components of the structure to form a two-dimensional network (Fig. 2 and Table-2).

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