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NOTE

Synthesis and Structural Characterization of 4-Hydroxyanilinium 3,4,5,6-Tetrabromo-2-(methoxycarbonyl)benzoate Methanol Monosolvate

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The compound, 4-hydroxyanilinium 3,4,5,6-tetrabromo-2-(methoxycarbonyl)benzoate methanol monosolvate ($C_{16}H_{15}NO_6Br_4$, M_r = 636.93) was synthesized and characterized by single crystal X-ray diffraction. The crystal belongs to triclinic, space group P-1, with a = 7.0403(9), b = 10.8695(12), c = 13.9844(16) Å, β = 82.852(2)°, V = 1033.4(2) Å^3, Z = 2, D_c = 2.047 g/cm^3. The final refinement gave R = 0.1051, wR(F^2) = 0.2658 for 3,482 observed reflections with I > 2σ(I). The asymmetric unit of the title compound contains one 4-hydroxyanilinium cation, one 3,4,5,6-tetrabromo-2-(methoxycarbonyl)benzoate anion and one methanol molecule. In the anion, the mean planes of the methoxycarbonyl and carboxylate groups form dihedral angles of 66.8 (3) and 88.8 (3)°, respectively with the benzene ring. In the crystal, intermolecular N---H...O and O---H...O hydrogen bonds connect the components of the structure to form a network.

Keywords: 4-Hydroxyanilinium 3,4,5,6-tetrabromo-2-(methoxycarbonyl)benzoate, Synthesis, X-Ray diffraction.

Tetrabromphthalimide and its derivatives have been found to be useful flame retardants in polyesters, *e.g.* polybutylene terephthalate and other resin formulations[1]. The several intermediates of them have been synthesized in the previous work[2,3]. In the present work, the reaction of tetrabromophthalic anhydride and 4-hydroxyaniline in methanol is expected to form 4,5,6,7-tetrabromo-2-(4-hydroxyphenyl)isoindoline-1,3-dione, but instead formed the title compound. In this paper, the synthesis and the crystal structure of the title compound is reported.

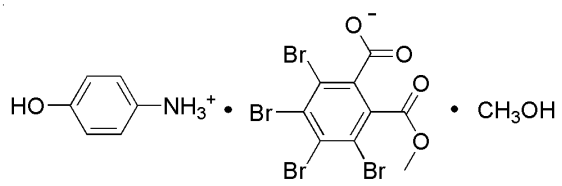
Synthesis of the title compound: All the reagents were of AR grade and used without further purification. A mixture of 4,5,6,7-tetrabromoisobenzofuran-1,3-dione (4.64 g, 0.01 mol) and methanol (15 mL) was refluxed for 0.5 h. Then 4-hydroxyaniline (1.09 g, 0.01 mol) was added to the above solution and mixed round for 0.5 h at room temperature. The solution was kept at room temperature for 6 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_α (λ = 0.71073 Å) radiation with an ω-2θ scan mode. The total reflections were 4,969 with 3,482 independent ones (R_{int} = 0.0550), of which 285 were observed with I > 2σ(I). Intensities were corrected for Lorentz and polarization effects and empirical absorption and all data were corrected using SADABB[7] program.

The structure was solved by direct methods using SHELXS-97[8] 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 crystallography[9]. The final least-square cycle gave R = 0.1051 and ωR = 0.2658 (w = $1/[\sigma^2(Fo^2) + (0.1809P)^2 + 0.0000P]$, where $P = (Fo^2 + 2Fc^2)/3$). S = 1.015, $(\Delta\rho)_{min}$ = -1.354 and $(\Delta\rho)_{max}$ = 4.926 e/Å^3. CIF file containing complete information on the studied structure was deposited with CCDC, deposition number 856011 and is freely available upon request from the following web site: www.ccdc.cam.ac.uk/data_request/cif.

In the present work, the reaction of 3,4,5,6-tetrabromo-2-(methoxycarbonyl)benzoic acid and 4-hydroxyaniline in methanol is expected to form 4,5,6,7-tetrabromo-2-(4-hydroxyphenyl) isoindoline-1,3-dione, but instead formed the title compound (**Scheme-I**). This may have happened because of the short time and cool temperature for the reaction.

The selected bond distances and bond angles are listed in Table-1. A displacement ellipsoid plot with atomic numbering



Scheme-I: Chemical structural formula of the title compound

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

Bond	Length (Å)	Bond	Angle (º)
Br(1)-C(5)	1.898(13)	C(1)-O(1)-C(9)	109(4)
Br(2)-C(6)	1.876(13)	O(1)-C(1)-O(2)	121(6)
Br(3)-C(7)	1.887(14)	O(1)-C(1)-C(3)	126(4)
Br(4)-C(8)	1.912(14)	O(2)-C(1)-C(3)	114(5)
N(1)-C(13)	1.504(16)	O(4)-C(2)-O(3)	123.3(14)
O(1)-C(1)	1.23(7)	O(4)-C(2)-C(4)	118.7(14)
O(1)-C(9)	1.44(4)	O(3)-C(2)-C(4)	118.0(14)
O(2)-C(1)	1.26(7)	O(5)-C(10)-C(11)	122.1(13)
O(3)-C(2)	1.250(18)	O(5)-C(10)-C(15)	117.0(13)
O(4)-C(2)	1.225(19)	C(12)-C(13)-N(1)	117.6(12)
O(5)-C(10)	1.363(17)	C(14)-C(13)-N(1)	115.5(12)

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, °) are listed in Table-2.

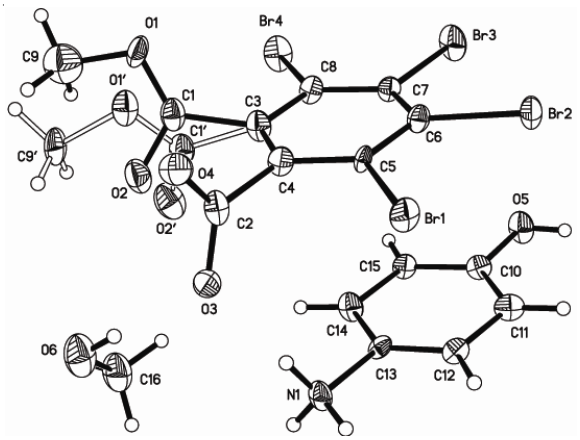


Fig. 1. Molecular structure with atomic numbering scheme

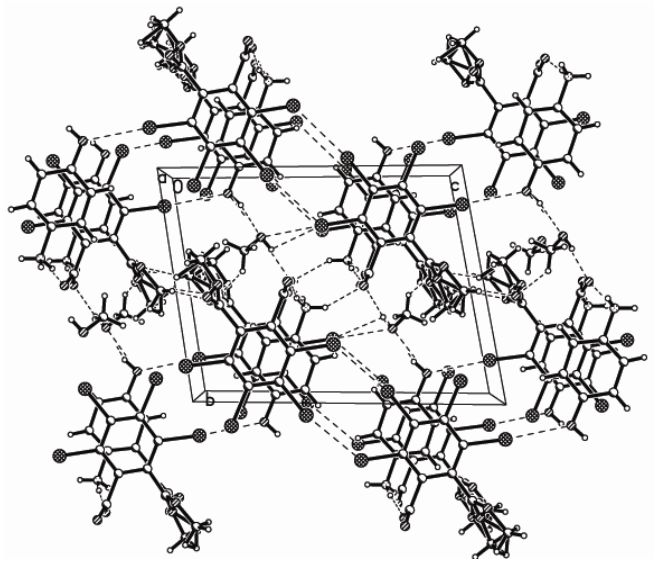


Fig. 2. View of crystal packing down the a-axis

TABLE-2
HYDROGEN BOND SCHEMES (Å, º)

D-H…A	D-H	H…A	D-A	D-H…A
N1-H1A…O4^{i}	0.89	2.194	2.992	149.0
N1-H1A…O3^{ii}	0.89	2.477	3.123	129.8
N1-H1B…O4^{iii}	0.89	1.940	2.783	157.5
N1-H1C…O3	0.89	1.934	2.820	174.2
O5-H5…O6^{iiii}	0.82	1.911	2.688	157.8
O6-H6…O3	0.82	1.955	2.769	171.8

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

The asymmetric unit of the title compound contains one 4-hydroxyanilinium cation, one 3,4,5,6-tetrabromo-2-(methoxycarbonyl)benzoate anion and one methanol molecule. In the anion, the mean planes of the methoxycarbonyl and carboxylate groups form dihedral angles of 66.8 (3) and 88.8 (3)°, respectively with the benzene ring. And the methoxycarbonyl group is disordered. The bond lengths and angles are in agreement with those in propan-1-aminium 3,4,5,6-tetra-bromo-2-(methoxycarbonyl)benzoate *N*,*N*-dimethylform-amide monosolvate[4], 2-methylanilinium 3,4,5,6-tetrabromo-2-(methoxy-carbonyl)benzoate methanol monosolvate[5] and in ethane-1,2-diammonium *bis*[2-(methoxy-carbonyl)-3,4,5,6-tetrabromobenzoate] methanol solvate[6]. In the crystal, intermolecular N---H...O and O---H...O hydrogen bonds connect the components of the structure to form a network (Fig. 2 and Table-2).

Conclusion

4-Hydroxyanilinium 3,4,5,6-tetrabromo-2-(methoxycarbonyl)benzoate methanol monosolvate ($C_{16}H_{15}NO_6Br_4$, M_r = 636.93) was synthesized by 'one pot'. X-ray diffraction analysis reveals that the title compound contains one cation, one anion and one methanol molecule. In the anion, the mean planes of the methoxycarbonyl and carboxylate groups form dihedral angles of 66.8 (3) and 88.8 (3)°, respectively with the benzene ring. The crystal belongs to triclinic with space group P-1. In the crystal, intermolecular N---H...O and O---H...O hydrogen bonds connect the components of the structure to form a network.

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