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NOTE

Synthesis and Crystal Structure of 5-Bromoisophthalic Acid

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A new compound *viz.*, 5-bromoisophthalic acid with the molecular formula $C_8H_7BrO_5$ has been successfully synthesized by the reaction of isophthalic acid and N-bromosuccinimide (NBS). The compound has been characterized by X-ray single-crystal diffraction and shows a one-dimensional framework. The 3D supramolecular structure is formed *via* hydrogen bonding connection.

Keywords: Coordination polymer, Crystal structure, Isophthalic acid.

Brominated benzene compounds have received wide attention as precursors in the synthesis of a variety of active pharmaceutical ingredients, for example, citalopram, bromperidol, bromindione, ambroxol, tramadol[1-3], *etc*. Also the bromarenes have been extensively used in the aromatic bond formation reactions such as Heck arylation, Suzuki, Buchwald, Negishi and Stille couplings[4], *etc*. for the synthesis of biaryls some of which are the precursors for a few of the antihypertensive agents. Bromoaromatic compounds find application in the synthesis of dendrimers. Several procedures are available for the synthesis of deactivated bromoarenes.

All reagent and solvents employed were commercially available and used as received without further purification.

General procedure: 5-Bromoisophthalic acid was prepared under the hydrothermal conditions. A mixture of isophthalic acid (16.6 mg, 0.1 mmol), H_2SO_4 (9.8 mg, 0.2 mmol) and N-bromosuccinimide (NBS) (14.13 mg, 0.1 mmol), H_2O (12 mL) was sealed into a 25 mL stainless steel reactor with a Teflon liner and heated at 333 K for 20 h. The reactor was then cooled slowly to room temperature and the solution filtered. Yellow block-shaped crystals were obtained from the filtrate after several days at room temperature. The yellow crystals suitable for X-ray diffraction analysis were collected.

Diffraction intensity data of the single crystal of the compound were collected on a Bruker SMART APEXII CCD diffractometer equipped with a graphite monochromated MoK_α radiation (λ = 0.71073 Å) by using a ω-scan mode. All the structures were solved by direct methods and refined by full-matrix least-squares methods on F^2 using the program SHELXL 97[5]. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were located by geometrically calculations and their positions and thermal parameters were fixed during the structure refinement. The crystallographic data and experimental details of structural analyses for coordination polymers are summarized in Table-1. Selected bond and angle parameters are listed in Table-2. CCDC: 911478.

TABLE-1
CRYSTALLOGRAPHIC DATA AND STRUCTURE REFINEMENT SUMMARY FOR 5-BROMOISOPHTHALIC ACID

Empirical formula	$C_8H_7BrO_5$	Z, Calculated density (mg/m^3)	4, 1.766
Formula weight	263.05	Absorption coefficient (mm^{-1})	4.147
Crystal system space group	Monoclinic, P2(1)/c	F(000)	520
Unit cell dimensions	a = 14.384(3) Å b = 9.626(2) Å c = 7.2062(16) Å	Limiting indices	-15 ≤ h ≤ 17 -11 ≤ k ≤ 11 -8 ≤ l ≤ 8
Volume (Å^3)	989.4(4)	Largest diff. peak and hole (e/Å^3)	1.000 and -0.691
θ Range for data collection	2.55 -25.50	Goodness-of-fit on F^2	1.184
Final R indices [I > 2σ(I)]	R_1 = 0.0494, wR_2 = 0.1831	R indices (all data)	R_1 = 0.0530, wR_2 = 0.1864

TABLE-2
SELECTED BOND LENGTHS (Å) AND ANGLES (°) FOR 5-BROMOISOPHTHALIC ACID

Br(1)-C(1)	2.098(8)	O(4)-C(7)	1.222(10)
O(2)-C(8)	1.312(12)	O(5)-C(7)	1.312(10)
O(3)-C(8)	1.207(11)	C(3)-C(8)	1.498(12)
O(2)-C(8)-C(3)	114.3(7)	C(5)-C(7)	1.478(11)
O(3)-C(8)-C(3)	121.2(9)	C(2)-C(1)-Br(1)	120.2(6)
O(3)-C(8)-O(2)	124.5(9)	C(6)-C(1)-Br(1)	118.8(6)
O(5)-C(7)-C(5)	114.1(7)	C(1)-C(2)-C(3)	119.6(7)
O(4)-C(7)-C(5)	122.1(8)	C(2)-C(3)-C(4)	120.4(7)
O(4)-C(7)-O(5)	123.8(8)	C(2)-C(3)-C(8)	118.5(7)
C(1)-C(6)-H(6)	120.7	C(4)-C(3)-C(8)	121.0(8)

The molecule of the 5-bromoisophthalic acid shows the benzene ring which are approximately planar, but the whole molecule is not (Fig. 1). The molecular conformation is characterized by the Br(1)-C(1)-C(2)-C(3) torsion angles of 179.8(6)Å which clearly deviate from planarity there are two kinds of outer-molecular hydrogen bonds coordinated and uncoordinated water molecules are also, respectively connected with adjacent of 5-bromoisophthalic acid anions by outer-molecular hydrogen bonds (d(O(1)-H(1W)...O(4)) = 2.839(9)Å, d(O(1)-H(2W)...O(4)) = 2.891(10)Å, d(O(2)-H(2)...O(1)) = 2.593(9)Å), other coordinated water molecules without linking with uncoordinated water molecules, are connected with adjacent 5-bromo-isophthalic acid by a kinds of outer-molecular hydrogen bonds (d(O(5)-H(5)...O(3)) = 2.616(9) Å). In the molecule, the Br(1)-C(1) bond lengths are found to be 2.098(8) Å, in addition, which are nearly equal to other typical single bonds. The bond angles C(2)-C(1)-Br(1), C(6)-C(1)-Br(1) are 120.2(6) Å, 118.8(6) Å (Fig. 2).

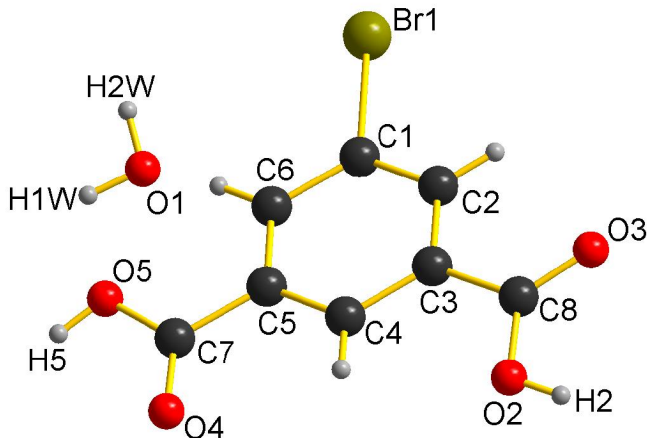

Fig. 1. Molecular structure of the title compound at 30 % probability displacement ellipsoids

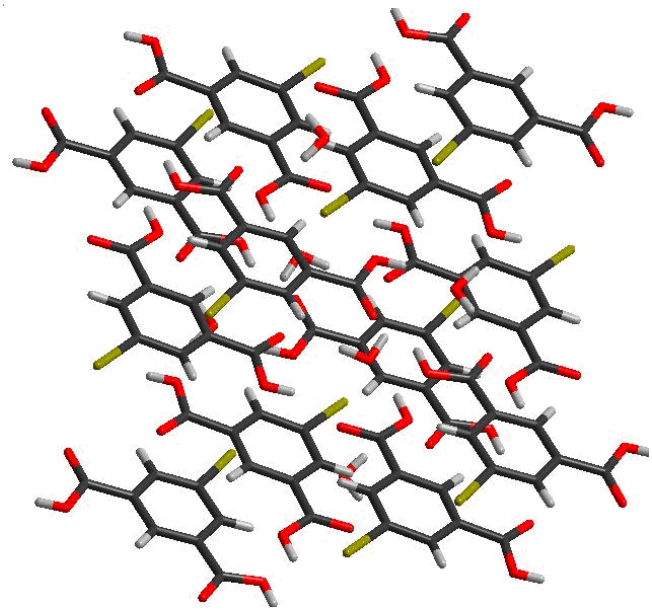

Fig. 2. 3D structure formed via hydrogen bonding interactions

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