

Hydrothermal Synthesis and Crystal Structure of 5-Aminoisophthalic acid with 4,4'-Bipyridine Forming Helical Chains *via* Hydrogen Bonds

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Co-crystallization of 5-aminoisophthalic acid with 4,4'-bipyridine was synthesized and characterized by single-crystal structure determination, IR and elemental analyses. The crystal is orthorhombic, space group *Pbca* with $a = 7.128(2)$, $b = 13.962(5)$, $c = 31.223(11)$ Å, $\alpha = \beta = \gamma = 90^\circ$, m.f. $C_{18}H_{15}N_3O_4$. $M_r = 337.33$, $V = 3107.3(18)$ Å³, $D_c = 1.442$ g/cm³, $F(000) = 1408$, $\mu = 0.104$ cm⁻¹ and $Z = 8$. The final refinement gave $R = 0.0607$ and $wR = 0.1406$ for 2096 reflections with $I > 2\sigma(I)$. Strong O–H...N hydrogen bonds connect the acid molecules with 4, 4'-bipyridine to form helical chain running along a crystallographic 2_1 axis in the c direction. The intermolecular π - π stacking interactions further assemble the architecture to form a supramolecular framework.

Key Words: 5-Aminoisophthalic acid, 4,4'-Bipyridine, Helical chain, Crystal structure.

INTRODUCTION

One of the most important targets in crystal engineering is rational design and preparation of compounds with desired design, topologies and functions¹⁻⁴. Members of the aromatic carboxylic acid family are widely used as versatile building blocks in both coordination polymer synthesis and the generation of hydrogen-bonding arrays of organic co-crystals. In contrast, 4,4'-bipyridine has been investigated in all branches of crystal engineering, from coordination polymers to non-covalent hydrogen-bonding adducts⁴⁻⁸. Whenever 4,4'-bipyridine takes part in the formation of co-crystals with organic molecules containing carboxyl groups, O–H...N hydrogen bonds are conventionally formed⁹.

As part of an investigation into O–H...N hydrogen bonds, we have produced co-crystals of 5-aminoisophthalic acid with 4,4'-bipyridine.

EXPERIMENTAL

Elemental analysis was carried out on a Carlo Erba 1106 full-automatic trace organic elemental analyzer. FT-IR spectra were recorded with a Bruker Equinox 55 FT-IR spectrometer in dry KBr pullet in the range of 4000-400 cm⁻¹.

Synthesis of the compound: A mixture of 5-aminoisophthalic acid (1 mmol), 4,4'-bipyridine (1 mmol) and distilled water (18 mL) was heated in a 25 mL stainless-steel reactor with a Teflon liner 160 °C for 96 h, followed by slow cooling to room temperature. Yellow crystals of the complex formed. Anal. calcd (%) for $C_{18}H_{15}N_3O_4$: C, 64.09; H, 4.48; N, 12.46. Found (%): C, 63.72; H, 4.38; N, 12.89. IR (KBr, cm^{-1}): 3569(w), 3011(w), 2995(w), 2242(m), 2160(vs), 1640(w), 1608(w), 1582(s), 1485(m), 1360(s), 1215(w), 1064(w), 850(w), 715(w), 692(m), 518(w).

Structure determination: A suitable yellow block crystal with dimensions of 0.20 mm \times 0.20 mm \times 0.15 mm was mounted on a glass fiber and the data were collected on a Bruker Smart 1000 CCD diffractometer with a MoK α radiation ($\lambda = 0.71073 \text{ \AA}$) at 293(2) K by using an ω scan mode in the range of $1.30 < \theta < 28.42^\circ$. For the title complex, a total of 19078 reflections were collected, of which 3852 were unique with $R_{int} = 0.0685$ ($-9 \leq h \leq 9$, $-18 \leq k \leq 18$, $-33 \leq l \leq 41$). All non-hydrogen atoms were located by direct methods and subsequent difference Fourier syntheses. The hydrogen atoms bound to carbon were located by geometrically calculations and their positions and thermal parameters were fixed during the structure refinement. All non-hydrogen atoms were refined by full-matrix least-squares techniques for observed 2096 reflections with $I > 2\sigma(I)$ to the final $R = 0.0607$, $wR = 0.1406$ ($w = 1/[\sigma^2(F_o)^2 + (0.0719P)^2 + 0.0950P]$, where $P = (F_o^2 + 2F_c^2)/3$), $S = 1.045$ and $(\Delta/\sigma)_{max} = 0.000$. The highest and lowest residual peaks in the final difference Fourier map are 0.195 and 0.225 $e/\text{\AA}^3$, respectively. All calculations were performed by the SHELXTL 97 program¹⁰. The selected bond lengths and bond angles are listed in Table-1. The molecular structure with atomic labeling scheme is shown in Fig. 1.

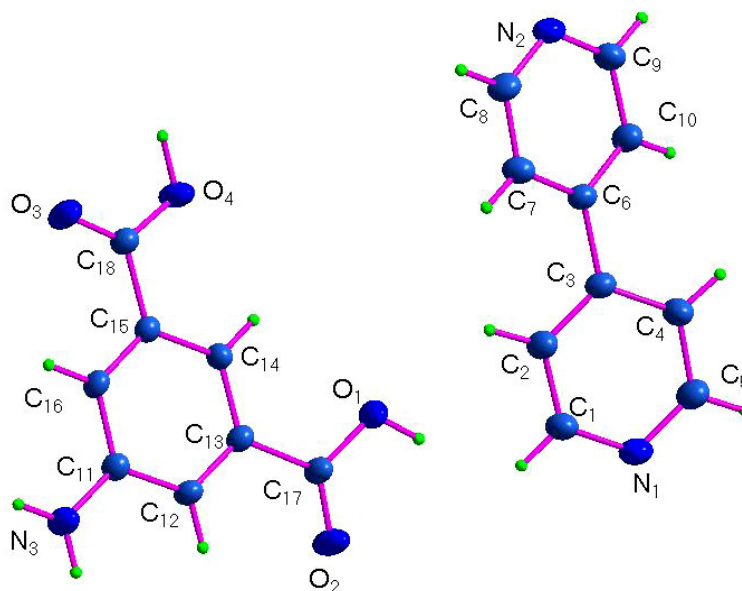


Fig. 1. Molecular structure for the title compound at 30 % probability displacement ellipsoids

TABLE-1
SELECTED BOND LENGTHS (Å) AND ANGLES (°) FOR COMPOUND

Bond	Dist.	Bond	Dist.
O(1)-C(17)	1.310(3)	N(2)-C(8)	1.327(3)
O(2)-C(17)	1.204(2)	N(2)-C(9)	1.329(3)
O(3)-C(18)	1.204(2)	C(1)-C(2)	1.382(3)
O(4)-C(18)	1.311(2)	C(3)-C(4)	1.384(3)
N(3)-C(11)	1.371(3)	C(3)-C(6)	1.485(3)
N(1)-C(1)	1.329(3)	C(4)-C(5)	1.373(3)
N(1)-C(5)	1.334(3)	C(6)-C(7)	1.389(3)
Angle	(°)	Angle	(°)
N(3)-C(11)-C(16)	121.03(18)	C(2)-C(3)-C(4)	116.5(2)
N(3)-C(11)-C(12)	121.10(19)	C(2)-C(3)-C(6)	122.1(2)
O(2)-C(17)-O(1)	122.35(19)	C(4)-C(3)-C(6)	121.4(2)
O(2)-C(17)-C(13)	123.00(2)	C(5)-C(4)-C(3)	119.8(2)
O(1)-C(17)-C(13)	114.64(19)	N(1)-C(5)-C(4)	123.5(2)
O(3)-C(18)-O(4)	122.88(19)	N(2)-C(8)-C(7)	123.6(2)
O(3)-C(18)-C(15)	123.50(2)	N(2)-C(9)-C(10)	123.3(2)
O(4)-C(18)-C(15)	113.61(18)		
C(1)-N(1)-C(5)	117.10(2)		
C(8)-N(2)-C(9)	117.01(19)		
N(1)-C(1)-C(2)	122.70(2)		

RESULTS AND DISCUSSION

The structure analysis reveals a 1:1 stoichiometry which is not consistent with the ratio of hydrogen-bonding donor and acceptor sites. The asymmetric unit of compound, which contain one formula unit, is depicted in Fig. 1. Bond lengths and angles agree with accepted values. Within each 4,4'-bipyridine subunit, the dihedral angle between the rings is 25.07°. For the 5-aminoisophthalic acid component, the carboxyl groups (O1-C17-O2 and O3-C18-O4) adopt *trans* arrangement in relation to the central benzene ring.

In the compound, there exist intermolecular hydrogen bonds between the O-H groups of 5-aminoisophthalic acid and the N atoms of 4,4'-bipyridine (Fig. 2 and Table-2). The hydrogen bond of O-H from 5-aminoisophthalic acid and N atoms from 4,4'-bipyridine form two kinds of intermolecular hydrogen bonds, with a distance of 1.65(3) Å (symmetry code: 1-x, -y, -z), a distance of 1.73(3) Å (symmetry code: -1/2+x, y, 1/2-z), a angle of 175(2)° and a angle of 175(3)°, which indicated that there are strong hydrogen bonds in the compound. The N atoms of 4,4'-bipyridine are bridged by V-shaped phthalic groups to form right-handed helical chains running along a crystallographic 2₁ axis in the C direction (Fig. 2). There also exist intermolecular hydrogen bonds between 5-aminoisophthalic acid molecules with a distance of 2.26 Å (symmetry code: x, 1-y, -z), a distance of 2.33 (symmetry code: 1/2-x, 1/2+y, z), a angle of 161° and a angle of 160°. The intermolecular π-π staking interactions

TABLE-2
PARAMETERS OF HYDROGEN-BONDING
INTERACTIONS IN THE TITLE COMPLEX

D-H...A	d(D-H)/Å	d(H...A)/Å	d(D...A)/Å	Angle (D-H...A)/°
O4-H1...N2#1	0.99(3)	1.65(3)	2.641(3)	175(2)
O1-H2...N1#2	0.90(3)	1.73(3)	2.635(3)	175(3)
N3-H3A...O3#3	0.86	2.26	3.081(3)	161
N3-H3B...O1#4	0.86	2.33	3.148(3)	160

Symmetry code: #1: 1-x,-y,-z; #2: -1/2+x,y,1/2-z; #3: -x,1-y,-z; #4: 1/2-x,1/2+y,z.

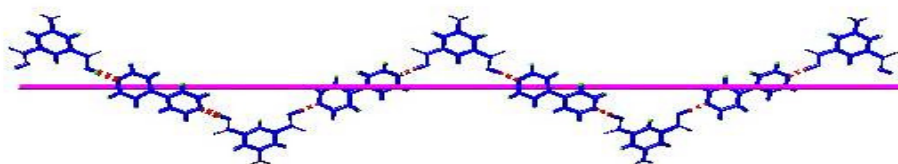


Fig. 2. Perspective views of the right-handed helical chains. The hydrogen bonds are indicated by dotted line

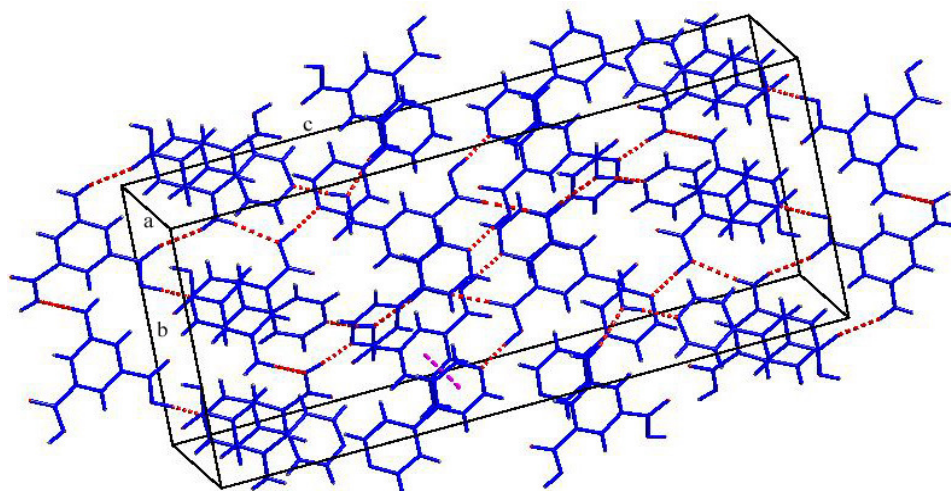


Fig. 3. Supramolecular network formed through hydrogen bonding and π - π stacking interactions

further assemble the architecture to form a supramolecular framework. The equation for the plane of Cg(1)(C11-C16) is $7.0377x + 0.803y - 4.62z = 0.734$ and the equation for the plane of Cg(3) (C6-C10, N2) is $7.112x + 0.323y + 1.96z = 6.347$. The interplanar Cg(1)- Cg(3) centroid distance is 3.617 Å (symmetry code: 1/2-x, 1/2+y, z), indicating the presence of face-to-face π - π stacking interactions that further stabilize the crystal structure and the corresponding dihedral angle is 6.75 °.

ACKNOWLEDGEMENTS

This work was supported by the National Natural Science Foundation of Shandong Province (No. Y2007F68) the Scientific Research Development Plan Project of Education Department of Shandong Province (J07WC09) and the Scientific Research Development Plan Project of DeZhou City (310543).

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(Received: 12 December 2008;

Accepted: 7 August 2009)

AJC-7733