Supplementary

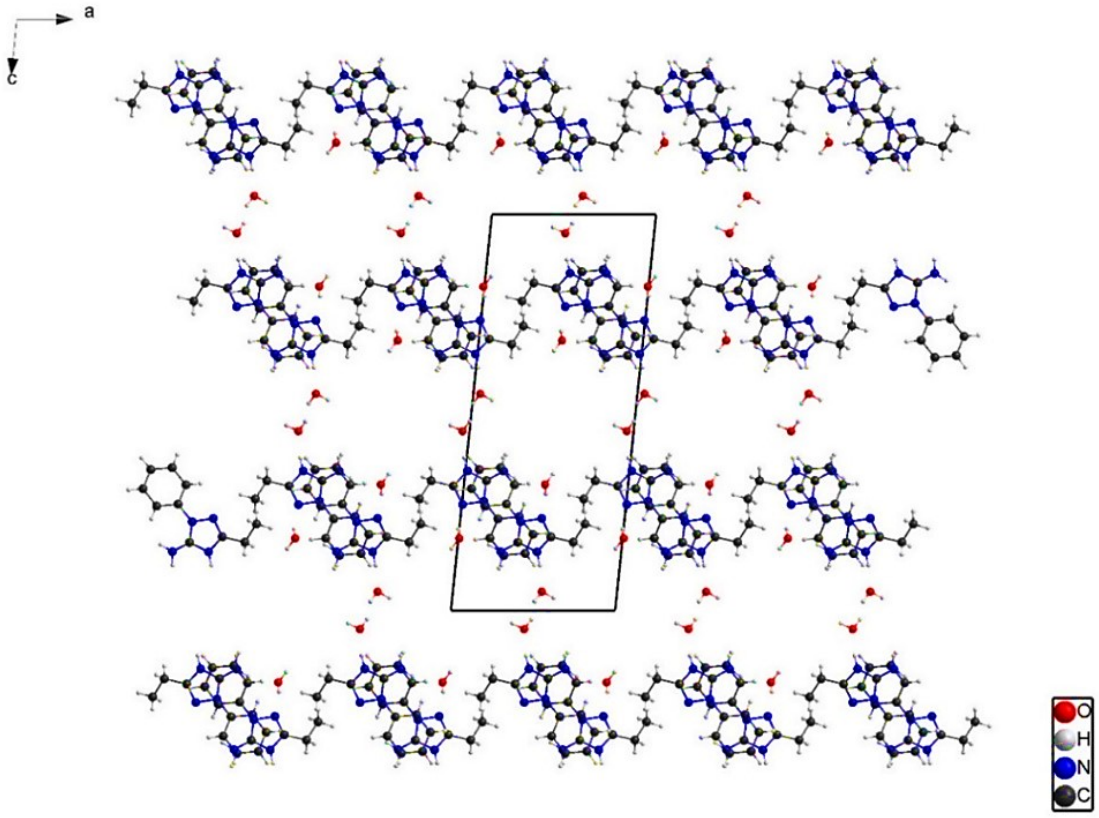

Fig. 1.S: The spatial arrangement of organic molecules within the unit cell

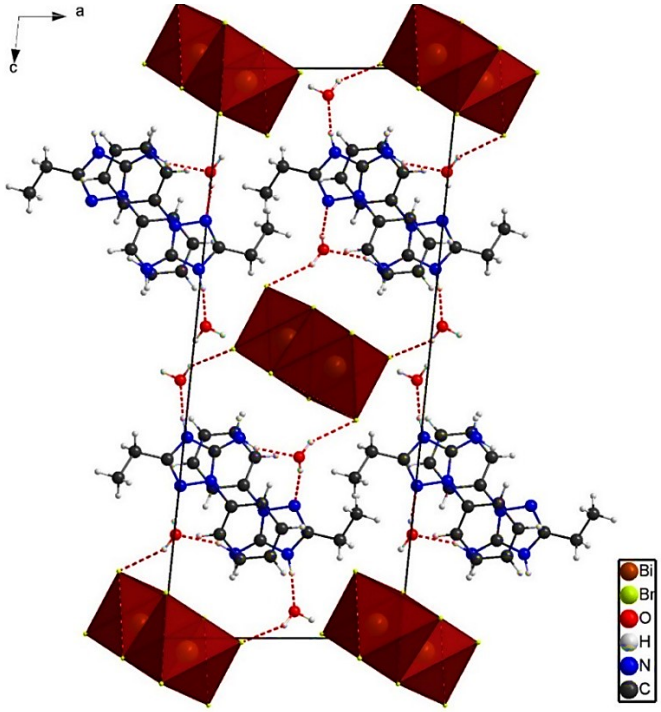

Fig. 2.S: Hydrogen bonding of the compound within the unit cell

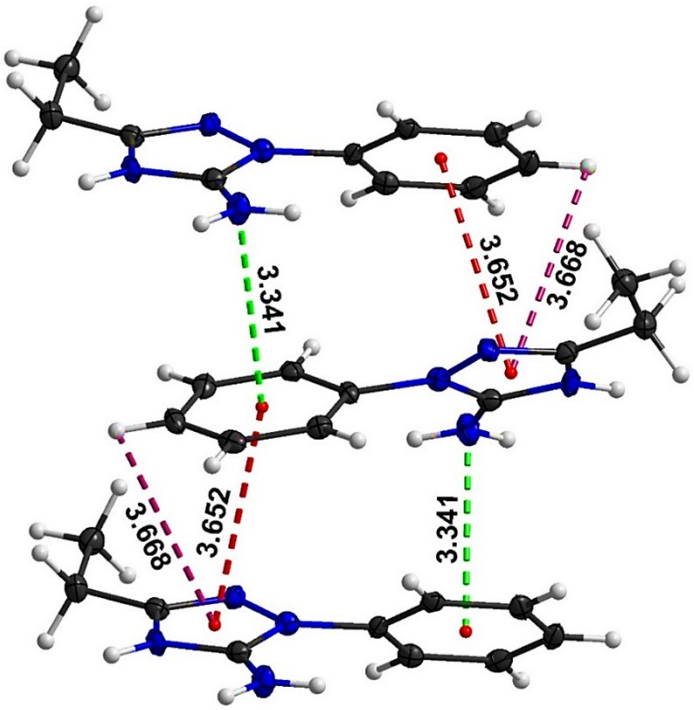

Fig. 3.S: Presence of different types of π Stacking in the Compound's Configuration

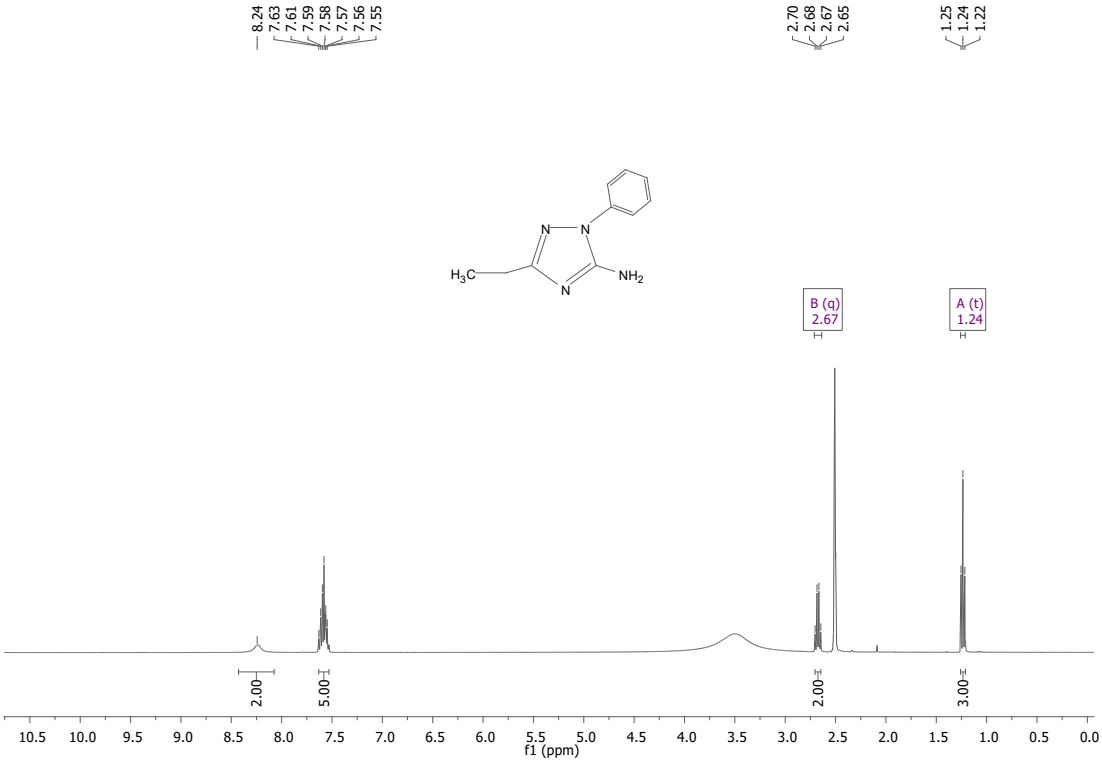

Fig. 4.S: NMR ^{1}H (400 MHz, DMSO-d_6)

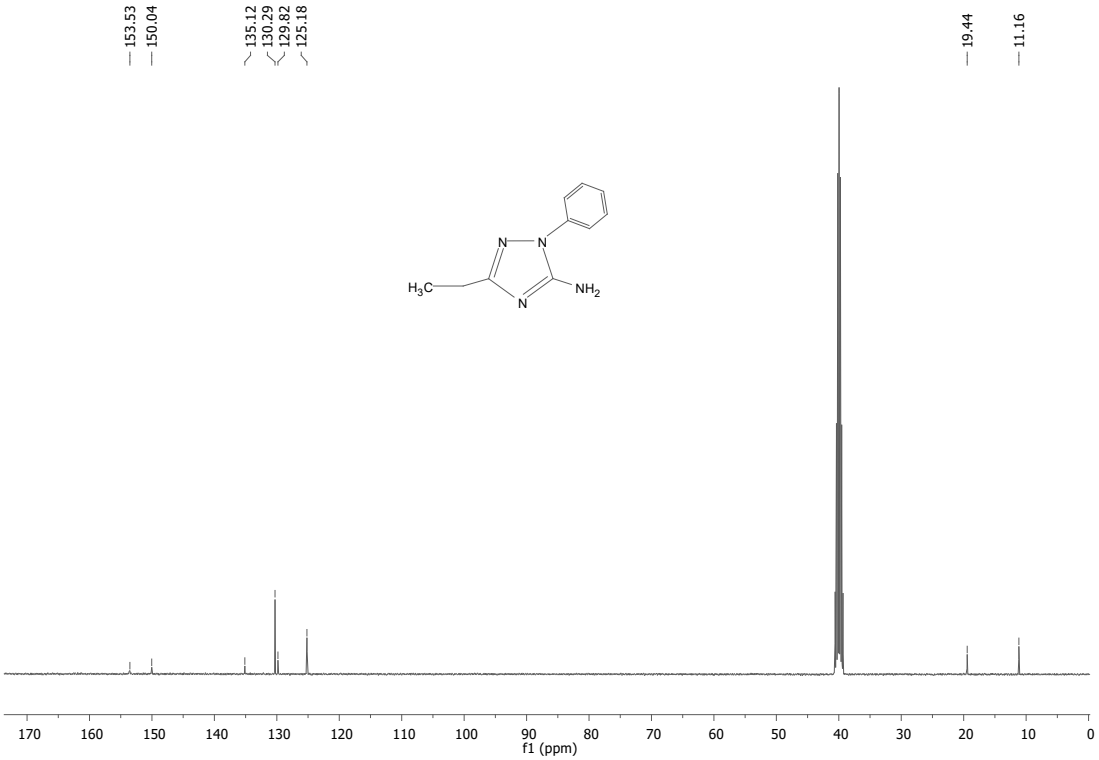

Fig. 5.S: NMR ^{13}C (100 MHz, DMSO-d_6)

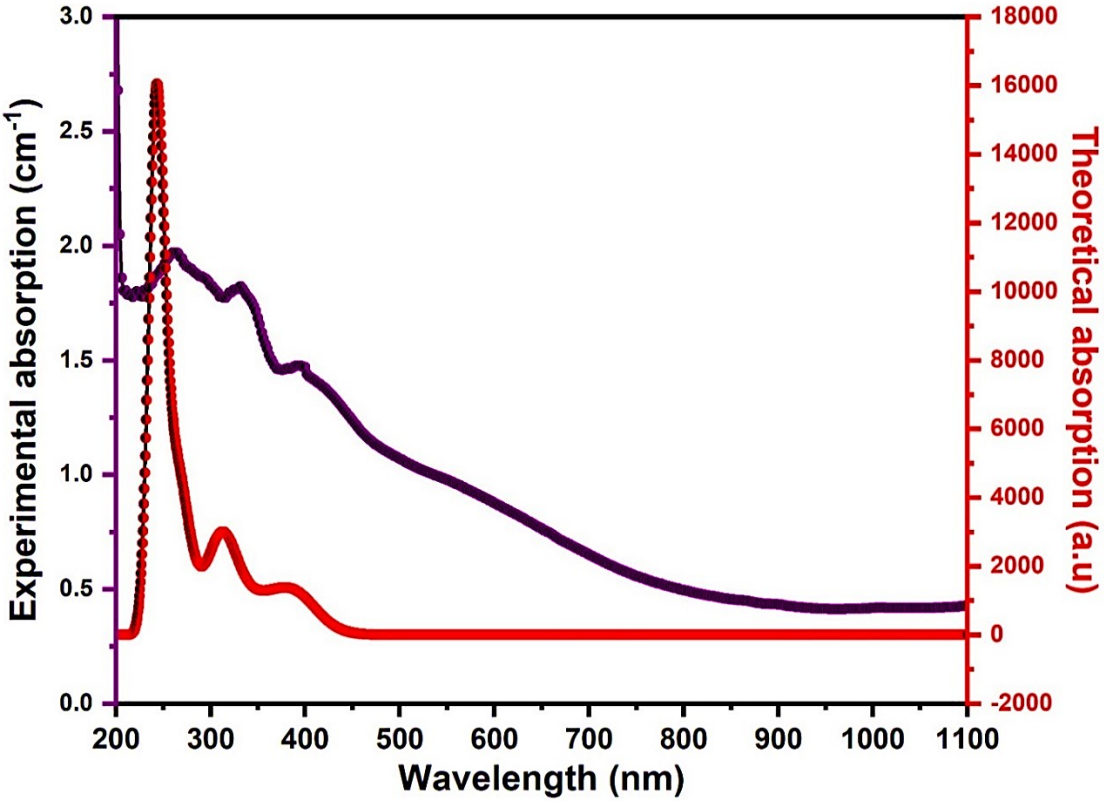

Fig. 6.S: Comparative Analysis of DFT and Experimental Absorption Profiles

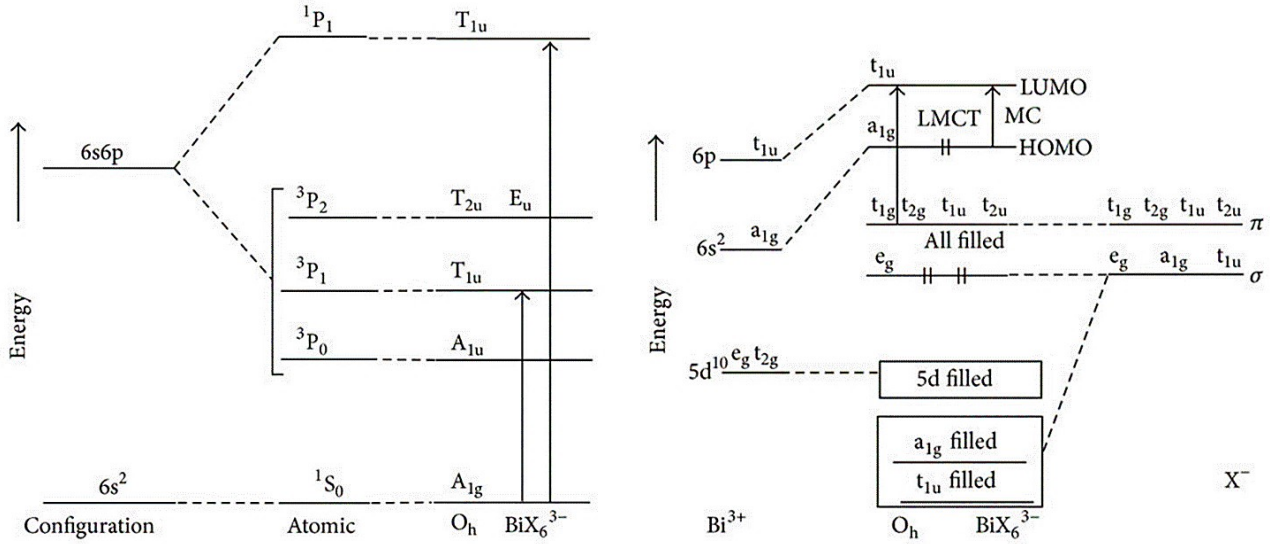

Fig. 7.S: (a) Atomic Term Splitting and Molecular Orbital Correlation Diagram of $(BiX_6)^{3-}$ ions, **(b)** Molecular Orbital Energy Level Diagram of $(BiX_6)^{3-}$ ions

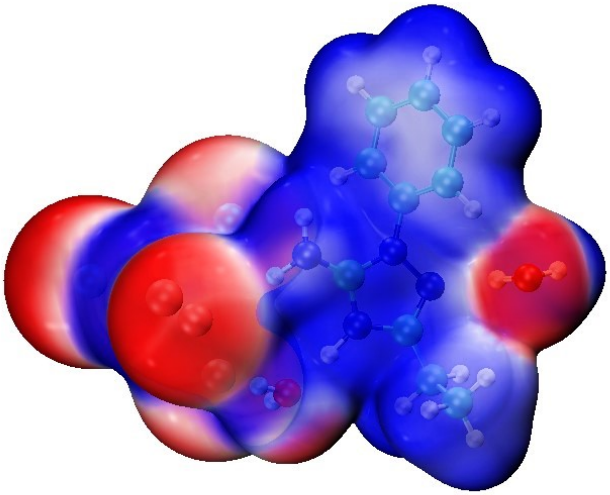

Fig. 8.S: Molecular Electrostatic Potential Analysis of the Target Compound

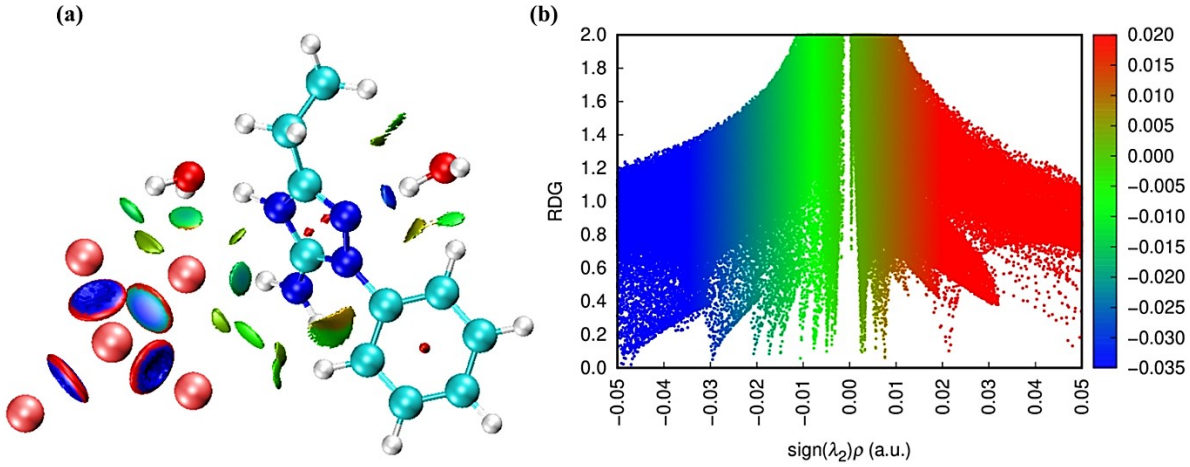

Fig. 9.S: (a) NCI and **(b)** RDG Visualization of the Target Compound

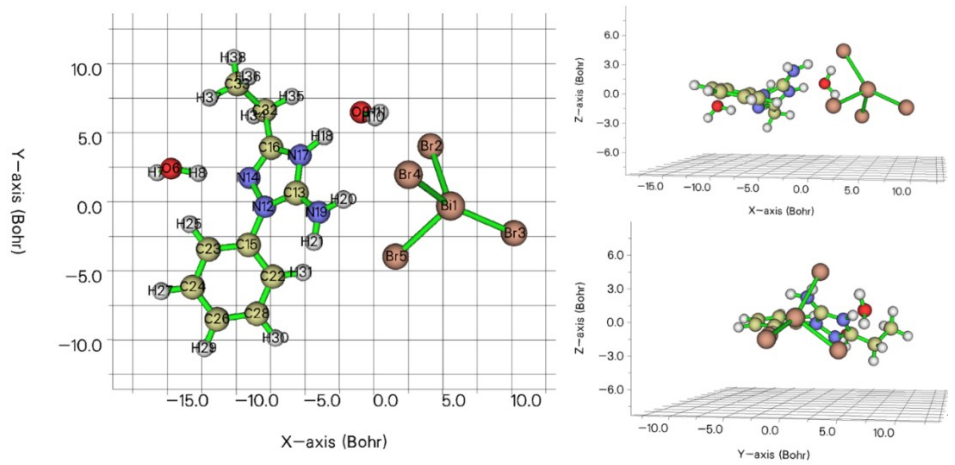

Fig. 10.S: Presentation of theoretical formula unit in (XY), (XZ), and (YZ)

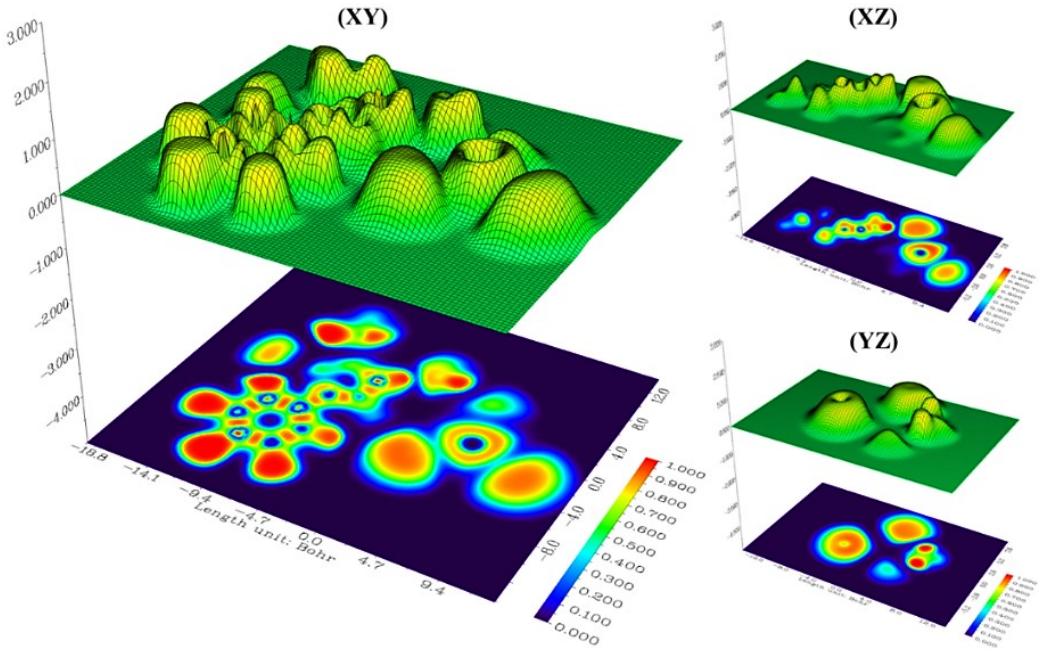

Fig. 11.S: Electron Localization Function (ELF) visualization in (XY), (XZ), and (YZ) planes

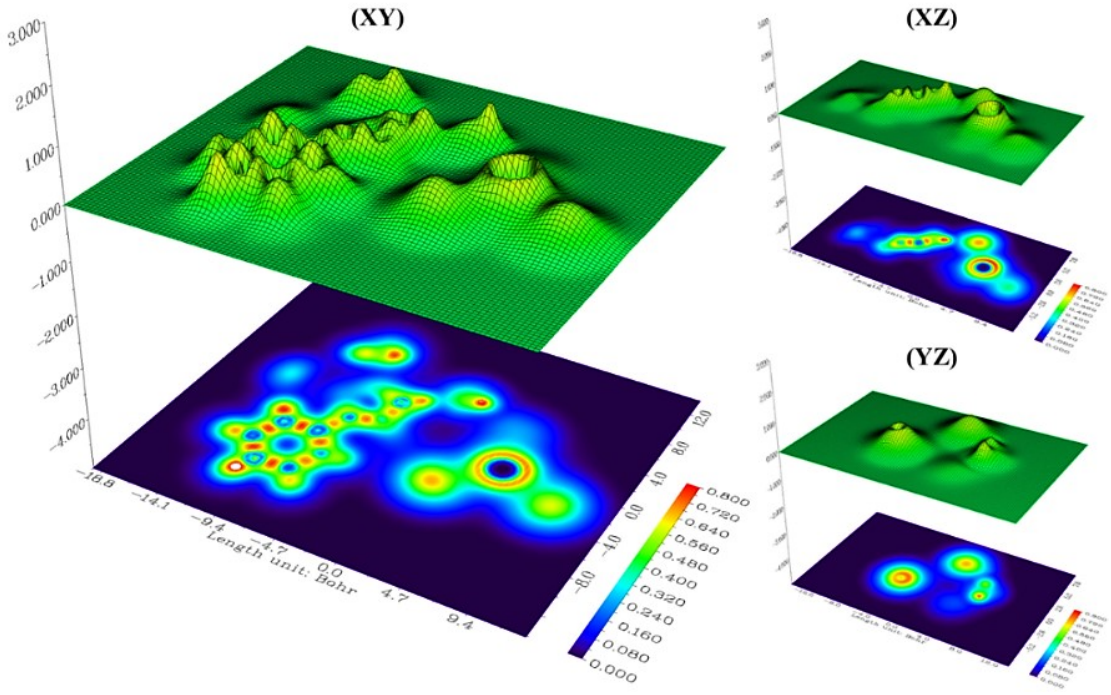

Fig. 12.S: Localized Orbital Locator (LOL) visualization in (XY), (XZ), and (YZ) planes

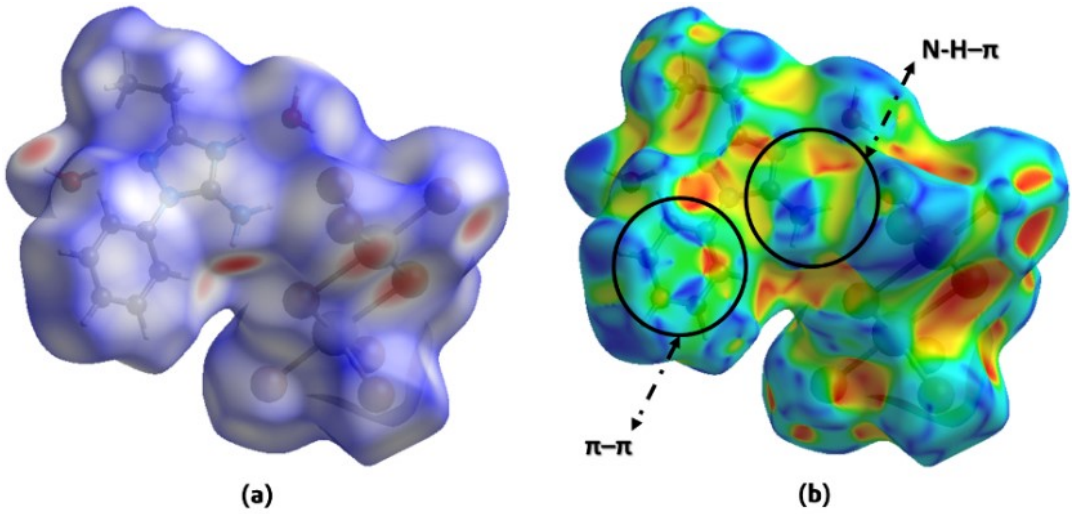

Fig. 13.S: Hirshfeld surface of the titled: **(a)** 3D dnorm surface, **(b)** surface index

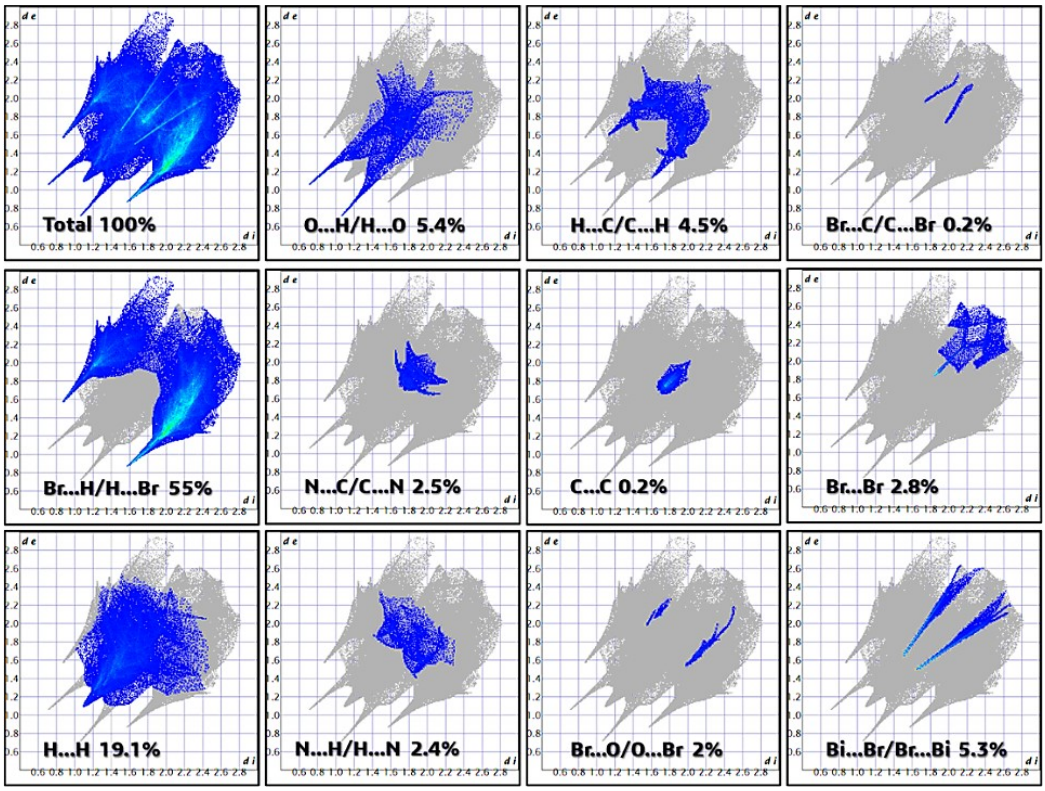

Fig. 14.S: 2D Visualization of Total Contact Contributions to the Hirshfeld Surface

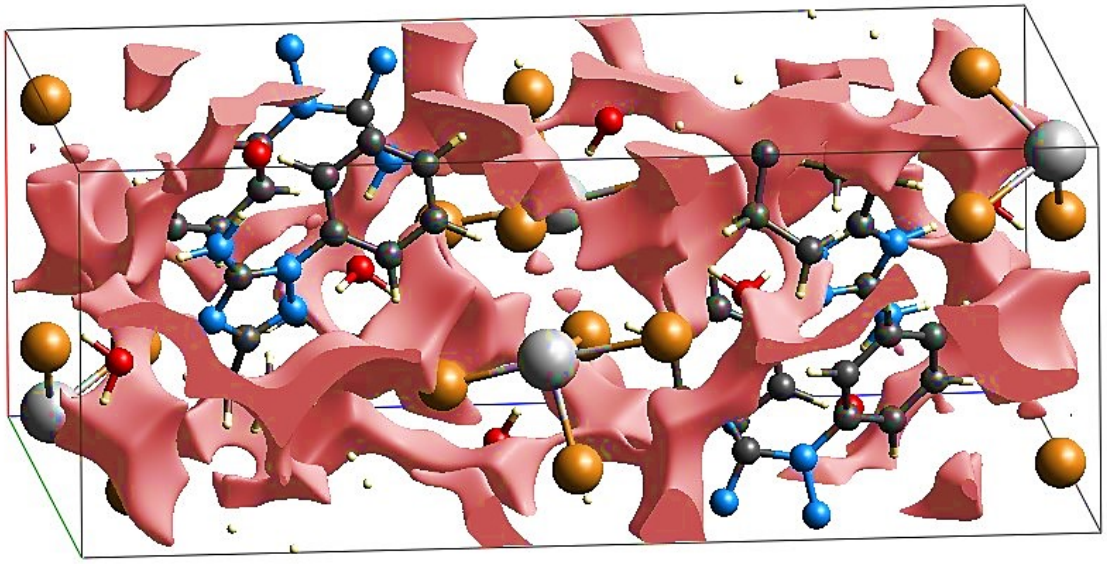

Fig. 15.S: Presence of a Crystal Void in the Compound

Table 1.S: Atomic coordinates and thermal agitation factors of the titled compound

	x	y	z	U_{iso}*/U_{eq}
Bi1	0.60523 (2)	0.23970 (2)	0.52392 (2)	0.01007 (5)
Br1	0.83185 (4)	0.08032 (5)	0.50732 (2)	0.01950 (9)
Br2	0.66286 (4)	0.55640 (5)	0.46466 (2)	0.01417 (8)

Br3	0.71889 (4)	0.38417 (5)	0.61753 (2)	0.01712 (9)
Br4	0.48995 (4)	0.06482 (5)	0.42005 (2)	0.01421 (8)
O1	0.9938 (3)	−0.1036 (4)	0.18190 (11)	0.0206 (6)
H1A	1.035740	−0.068735	0.156067	0.031*
H1B	1.004972	−0.019186	0.205138	0.031*
O2	1.0417 (3)	0.3752 (5)	0.45279 (12)	0.0276 (7)
H2A	1.117601	0.400347	0.467745	0.041*
H2B	1.004221	0.322001	0.477237	0.041*
N1	0.8689 (3)	0.2191 (4)	0.27603 (12)	0.0123 (6)
N2	0.9953 (3)	0.1606 (4)	0.26752 (13)	0.0137 (6)
N3	0.9874 (3)	0.2431 (4)	0.35235 (13)	0.0141 (7)
H3	1.013460	0.263570	0.385741	0.017*
N4	0.7669 (3)	0.3337 (5)	0.35177 (13)	0.0177 (7)
H4A	0.776883	0.360242	0.385587	0.021*
H4B	0.692021	0.348029	0.333483	0.021*
C1	0.7714 (4)	0.2373 (5)	0.23134 (14)	0.0113 (7)
C2	0.8076 (4)	0.3042 (5)	0.18256 (15)	0.0131 (7)
H2	0.894112	0.334650	0.179191	0.016*
C3	0.7127 (4)	0.3246 (5)	0.13926 (15)	0.0163 (8)
H3A	0.735547	0.370479	0.106722	0.020*
C4	0.5840 (4)	0.2772 (5)	0.14408 (16)	0.0177 (8)
H4	0.521184	0.290888	0.114724	0.021*
C5	0.5486 (4)	0.2095 (5)	0.19238 (16)	0.0162 (8)
H5	0.462091	0.178307	0.195387	0.019*
C6	0.6425 (4)	0.1881 (5)	0.23650 (15)	0.0138 (8)
H6	0.619330	0.141701	0.268922	0.017*
C7	0.8659 (4)	0.2713 (5)	0.32809 (16)	0.0147 (8)
C8	1.0626 (4)	0.1755 (5)	0.31414 (15)	0.0141 (8)
C9	1.2024 (4)	0.1245 (6)	0.32752 (17)	0.0205 (9)
H9A	1.209585	0.045315	0.358767	0.025*
H9B	1.252594	0.233044	0.337201	0.025*
C10	1.2612 (4)	0.0301 (6)	0.28160 (17)	0.0211 (9)
H10A	1.254319	0.107484	0.250440	0.032*
H10B	1.214883	−0.080727	0.272974	0.032*

H10C	1.351525	0.003800	0.292314	0.032*

Table 2.S: Distances and angles of chemical bonds in $[BiBr_4]_n^-$ anions.

Distances (Å)	
Bi1—Br1	2.6812 (4)
Bi1—Br2^{i}	3.1803 (4)
Bi1—Br2	2.8596 (4)
Bi1—Br3	2.7151 (4)
Bi1—Br4	3.0211 (4)
Bi1—Br4^{ii}	2.8708 (4)

Angles (°)	
Br1—Bi1—Br2^{i}	175.782 (12)
Br1—Bi1—Br2	92.848 (12)
Br1—Bi1—Br3	90.024 (12)
Br1—Bi1—Br4	87.208 (12)
Br1—Bi1—Br4^{ii}	94.392 (12)
Br2—Bi1—Br2^{i}	83.496 (11)
Br2—Bi1—Br4	89.542 (11)
Br2—Bi1—Br4^{ii}	172.061 (12)
Br3—Bi1—Br2	91.580 (12)
Br3—Bi1—Br2^{i}	92.175 (11)
Br3—Bi1—Br4^{ii}	91.672 (12)
Br3—Bi1—Br4	177.061 (12)
Br4—Bi1—Br2^{i}	90.650 (11)
Br4^{ii}—Bi1—Br2^{i}	89.144 (11)
Br4^{ii}—Bi1—Br4	87.562 (10)
Bi1—Br2—Bi1^{i}	96.503 (11)
Bi1^{ii}—Br4—Bi1	92.437 (10)

Table 3.S: Interatomic distances and chemical bond angles in $(C_{10}H_{13}N_4)^+$ cations.

Distances (Å)	
O1—H1A	0.8502
O1—H1B	0.8503
O2—H2A	0.8500
O2—H2B	0.8496
N1—N2	1.407 (4)
N1—C1	1.426 (5)
N1—C7	1.355 (5)
N2—C8	1.293 (5)
N3—H3	0.8600
N3—C7	1.347 (5)
N3—C8	1.380 (5)
N4—H4A	0.8600
N4—H4B	0.8600
N4—C7	1.312 (5)
C1—C2	1.397 (5)
C1—C6	1.394 (5)
C2—H2	0.9300
C2—C3	1.386 (5)
C3—H3A	0.9300
C3—C4	1.386 (6)
C4—H4	0.9300
C4—C5	1.385 (6)
C5—H5	0.9300
C5—C6	1.394 (5)
C6—H6	0.9300
C8—C9	1.490 (5)
C9—H9A	0.9700
C9—H9B	0.9700
C9—C10	1.517 (6)
C10—H10A	0.9600
C10—H10B	0.9600

C10—H10C	0.9600

Angles (°)	
H1A—O1—H1B	104.4
H2A—O2—H2B	104.6
N2—N1—C1	119.9 (3)
C7—N1—N2	110.1 (3)
C7—N1—C1	129.5 (3)
C8—N2—N1	104.8 (3)
C7—N3—H3	126.1
C7—N3—C8	107.9 (3)
C8—N3—H3	126.1
H4A—N4—H4B	120.0
C7—N4—H4A	120.0
C7—N4—H4B	120.0
C2—C1—N1	118.8 (3)
C6—C1—N1	120.2 (3)
C6—C1—C2	120.9 (3)
C1—C2—H2	120.5
C3—C2—C1	119.0 (4)
C3—C2—H2	120.5
C2—C3—H3A	119.8
C2—C3—C4	120.5 (4)
C4—C3—H3A	119.8
C3—C4—H4	119.8
C5—C4—C3	120.3 (4)
C5—C4—H4	119.8
C4—C5—H5	119.9
C4—C5—C6	120.1 (4)
C6—C5—H5	119.9
C1—C6—C5	119.1 (4)
C1—C6—H6	120.5
C5—C6—H6	120.5
N3—C7—N1	105.9 (3)
N4—C7—N1	128.7 (4)

N4—C7—N3	125.5 (4)
N2—C8—N3	111.3 (3)
N2—C8—C9	126.4 (4)
N3—C8—C9	122.3 (3)
C8—C9—H9A	108.9
C8—C9—H9B	108.9
C8—C9—C10	113.5 (3)
H9A—C9—H9B	107.7
C10—C9—H9A	108.9
C10—C9—H9B	108.9
C9—C10—H10A	109.5
C9—C10—H10B	109.5
C9—C10—H10C	109.5
H10A—C10—H10B	109.5
H10A—C10—H10C	109.5
H10B—C10—H10C	109.5

Table 4.S: The attributions of calculated and observed frequencies of the vibration modes of the compound

IR (cm^{-1})	Raman (cm^{-1})	Calc. wavenumbers (cm^{-1})	Assignment
3814	-	**3811**	υ_{as}**(H_2O)**
3736	-	**3687**	υ_{as}**(NH_2)**
3665	-	**3660**	υ_{as}**(H_2O)**
3558	-	**3544**	υ_{s}**(H_2O)**
3433	-	**3466**	υ_{s}**(H_2O)**
3392	-	**3363**	υ_{s}**(NH_2)**
3262	-	**3240**	υ_{s}**(C-H)** $_{\text{Benzene}}$
3142	-	**3161**	υ_{as}**(C-H)** $_{\text{Ethyl group}}$
3058	-	**3086**	υ_{s}**(CH_2)**
3022	-	**3053**	υ_{s}**(CH_3)**
2663	-	**2613**	**υ(N-H...O)**
1679	-	**1738**	**β(N-H)**
1590	-	**1633**	**δ(NH_2)**
1507	-	**1535**	**δ(CH_2)**
1484	-	**1490**	β_{as}**(C-H)** $_{\text{Benzene}}$

1457	**-**	**1447**	**ω(CH_3)**
1382	**-**	**1415**	**υ(C-N) + υ(C-C)**
1303	**-**	**1318**	**τ(CH_2) + τ(NH_2)**
1154	**-**	**1212**	**β_s(C-H) $_{Benzene}$**
1131	**-**	**1146**	**υ(N-N)**
1075	**-**	**1109**	**τ(CH_3)**
1034	**-**	**1052**	**γ_{as}(C-H) $_{Benzene}$**
968	**-**	**987**	**γ_{as}(C-H) $_{Benzene}$**
811	**-**	**822**	**ρ(CH_3)**
764	**-**	**802**	**γ_s(C-H) $_{Benzene}$**
732	**-**	**755**	**ω(NH_2)**
677	**-**	**677**	**ω(H_2O)**
620	**-**	**633**	**δ(C-C=C)**
565	**-**	**565**	**τ(H_2O)**
-	**183**	**186**	**υ_{as}(Bi-Br)**
-	**166**	**164**	**υ_s(Bi-Br)**
	131	**131**	**δ (Br-Bi-Br)**
	118	**113**	**δ (Br-Bi-Br)**
-	**90**	**84**	**$Bridge$ (Bi-Br)**
-	**75**	**68**	**Lattice Mode**

υ_s :$symetric\ stretching$, υ_{as} :$assymetric\ stretching$, β : $in\ plane\ bending$, γ :$out\ plane\ bending$, δ :$scissoring$, ρ :$rocking$,
ω:$wagging$, τ : Twisting

Table 5.S: Calculated global reactivity parameters of the new compound.

Parameter	Value (eV)
HOMO	-6.89
LUMO	-3.07
E_A	3.07
E_I	6.89
μ	-4.98
η	1.91
S	1.83
ω	6.49
χ	4.98