Manifestation of helicity in one-dimensional iodobismuthate

Souvik Pandey, Alex P. Andrews and Ajay Venugopal*

Supplementary Information

Experimental Methods

The reactions were performed under ambient conditions. $Bi(NO_3)_3(H_2O)_5$ and 2,6-diisopropylaniline were purchased from Sigma Aldrich and used as received. Elemental analysis was carried out on the vario MICRO cube elemental analyser. The FT-IR spectrum was recorded using KBr pellets in the range of 4000–400 cm^{-1} on a SHIMADZU FT-IR spectrometer. Thermogravimetric analysis (TGA) was performed using a SDT Q600 (Shimadzu) analyser under nitrogen flow and heating rate was maintained at 10 °C per minute. The diffuse reflectance spectra were recorded at room temperature on a computer-controlled Shimadzu UV/Vis/NIR spectrophotometer. A $BaSO_4$ plate was used as reference, on which the finely ground powders (5 % (w/w)) of the samples were coated. Optical band gaps were calculated from UV-Vis diffuse reflectance spectra using the Kubelka-Munk function where E = Energy, α = absorption coefficient, h = Planck's constant, ν = frequency.[1] Single-crystal X-ray crystallography for structural analysis was performed with a Bruker Kappa Apex-II CCD diffractometer at 296 K, 85 K and MoKα irradiation (λ = 0.71073 Å). The structures were solved by direct methods with SIR-92,[2] SHELXS-97, or SHELX-2013.[3] Powder XRD measurement was performed on a X'pert PRO (PANalytics) powder diffractometer equipped with Cu Kα radiation (1.540598 Å). Piezoelectric measurement was performed on D_{33} meter (APC International, part no. 902030). 1 mm thick pellets of compound **1** were used for the measurements. The cif files of the single crystal XRD measurements can be obtained from www.ccdc.cam.ac.uk/data_request/cif. CCDC 1468858 (**1** at 85K), CCDC 1468859 (**1** at 296 K).

Crystal data and structure refinement for 1.

Identification code	**1**	
Empirical formula	$C_{12}H_{20}BiI_4N$	
Formula weight	894.87	
Temperature	296(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	$C222_1$	
Unit cell dimensions	a = 17.363(2) Å	α= 90°.
	b = 24.704(3) Å	β= 90°.
	c = 9.8942(10) Å	γ = 90°.
Volume	4244.0(9) $Å^3$	
Z	8	
Density (calculated)	2.801 Mg/m^3	
Absorption coefficient	14.117 mm^{-1}	
F(000)	3152	
Crystal size	0.150 x 0.100 x 0.100 mm^3	
Theta range for data collection	2.638 to 25.000°.	
Index ranges	-18<=h<=20, -29<=k<=26, -11<=l<=11	
Reflections collected	9045	
Independent reflections	3730 [R(int) = 0.0276]	
Completeness to theta = 25.242°	97.6 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.333 and 0.226	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3730 / 5 / 168	
Goodness-of-fit on F2	0.890	
Final R indices [I>2σ(I)]	R1 = 0.0286, wR2 = 0.0570	
R indices (all data)	R1 = 0.0440, wR2 = 0.0618	
Absolute structure parameter	0.057(7)	
Largest diff. peak and hole	1.347 and -0.609 e.$Å^{-3}$	

Table T1: Bond lengths [Å] and angles [°] for 1.

C(1)-C(2)	1.328(16)
C(1)-C(2)#1	1.328(16)

C(1)-N(1)	1.51(2)
C(2)-C(3)	1.46(2)
C(2)-C(5)	1.606(17)
C(3)-C(4)	1.34(2)
C(3)-H(3)	0.9300
C(4)-C(3)#1	1.34(2)
C(4)-H(4)	0.9300
C(5)-C(6)	1.501(12)
C(5)-C(7)	1.51(2)
C(5)-H(5)	0.9800
C(6)-H(6A)	0.9600
C(6)-H(6B)	0.9600
C(6)-H(6C)	0.9600
C(7)-H(7A)	0.9600
C(7)-H(7B)	0.9600
C(7)-H(7C)	0.9600
C(8)-C(9)	1.370(16)
C(8)-C(9)#2	1.370(16)
C(8)-N(2)	1.51(2)
C(9)-C(10)	1.40(2)
C(9)-C(12)	1.632(19)
C(10)-C(11)	1.357(19)
C(10)-H(10)	0.9300
C(11)-C(10)#2	1.357(19)
C(11)-H(11)	0.9300
C(12)-C(13)	1.513(12)
C(12)-C(14)	1.47(2)
C(12)-H(12)	0.9800
C(13)-H(13A)	0.9600
C(13)-H(13B)	0.9600
C(13)-H(13C)	0.9600
C(14)-H(14A)	0.9600
C(14)-H(14B)	0.9600
C(14)-H(14C)	0.9600
N(1)-H(1A)	0.8900
N(1)-H(1B)	0.8900

N(1)-H(1C)	0.8900
N(2)-H(2A)	0.8900
N(2)-H(2B)	0.8900
N(2)-H(2C)	0.8900
I(1)-Bi(3)	3.0674(10)
I(1)-Bi(3)#3	3.3879(10)
I(2)-Bi(3)	2.8822(11)
I(3)-Bi(3)	2.8969(13)
I(4)-Bi(3)	3.0803(9)
I(4)-Bi(3)#4	3.3819(12)
Bi(3)-I(4)#4	3.3819(12)
Bi(3)-I(1)#3	3.3878(10)

C(2)-C(1)-C(2)#1	129.8(19)
C(2)-C(1)-N(1)	115.1(9)
C(2)#1-C(1)-N(1)	115.1(9)
C(1)-C(2)-C(3)	114.0(15)
C(1)-C(2)-C(5)	128.1(15)
C(3)-C(2)-C(5)	118.0(15)
C(4)-C(3)-C(2)	120(2)
C(4)-C(3)-H(3)	119.9
C(2)-C(3)-H(3)	119.9
C(3)-C(4)-C(3)#1	122(3)
C(3)-C(4)-H(4)	119.1
C(3)#1-C(4)-H(4)	119.1
C(6)-C(5)-C(7)	113.3(16)
C(6)-C(5)-C(2)	107.8(13)
C(7)-C(5)-C(2)	111.0(13)
C(6)-C(5)-H(5)	108.2
C(7)-C(5)-H(5)	108.2
C(2)-C(5)-H(5)	108.2
C(5)-C(6)-H(6A)	109.5
C(5)-C(6)-H(6B)	109.5
H(6A)-C(6)-H(6B)	109.5
C(5)-C(6)-H(6C)	109.5
H(6A)-C(6)-H(6C)	109.5

H(6B)-C(6)-H(6C)	109.5
C(5)-C(7)-H(7A)	109.5
C(5)-C(7)-H(7B)	109.5
H(7A)-C(7)-H(7B)	109.5
C(5)-C(7)-H(7C)	109.5
H(7A)-C(7)-H(7C)	109.5
H(7B)-C(7)-H(7C)	109.5
C(9)-C(8)-C(9)#2	127.5(19)
C(9)-C(8)-N(2)	116.3(10)
C(9)#2-C(8)-N(2)	116.3(10)
C(8)-C(9)-C(10)	114.6(16)
C(8)-C(9)-C(12)	124.6(14)
C(10)-C(9)-C(12)	120.8(14)
C(11)-C(10)-C(9)	120.4(19)
C(11)-C(10)-H(10)	119.8
C(9)-C(10)-H(10)	119.8
C(10)#2-C(11)-C(10)	122(3)
C(10)#2-C(11)-H(11)	118.9
C(10)-C(11)-H(11)	118.9
C(13)-C(12)-C(14)	115.0(18)
C(13)-C(12)-C(9)	102.7(13)
C(14)-C(12)-C(9)	111.2(16)
C(13)-C(12)-H(12)	109.3
C(14)-C(12)-H(12)	109.3
C(9)-C(12)-H(12)	109.3
C(12)-C(13)-H(13A)	109.5
C(12)-C(13)-H(13B)	109.5
H(13A)-C(13)-H(13B)	109.5
C(12)-C(13)-H(13C)	109.5
H(13A)-C(13)-H(13C)	109.5
H(13B)-C(13)-H(13C)	109.5
C(12)-C(14)-H(14A)	109.5
C(12)-C(14)-H(14B)	109.5
H(14A)-C(14)-H(14B)	109.5
C(12)-C(14)-H(14C)	109.5
H(14A)-C(14)-H(14C)	109.5

H(14B)-C(14)-H(14C)	109.5
C(1)-N(1)-H(1A)	109.5
C(1)-N(1)-H(1B)	109.5
H(1A)-N(1)-H(1B)	109.5
C(1)-N(1)-H(1C)	109.5
H(1A)-N(1)-H(1C)	109.5
H(1B)-N(1)-H(1C)	109.5
C(8)-N(2)-H(2A)	109.5
C(8)-N(2)-H(2B)	109.5
H(2A)-N(2)-H(2B)	109.5
C(8)-N(2)-H(2C)	109.5
H(2A)-N(2)-H(2C)	109.5
H(2B)-N(2)-H(2C)	109.5
Bi(3)-I(1)-Bi(3)#3	90.50(2)
Bi(3)-I(4)-Bi(3)#4	91.43(3)
I(2)-Bi(3)-I(3)	95.44(4)
I(2)-Bi(3)-I(1)	91.22(3)
I(3)-Bi(3)-I(1)	96.44(4)
I(2)-Bi(3)-I(4)	96.65(3)
I(3)-Bi(3)-I(4)	91.04(3)
I(1)-Bi(3)-I(4)	168.59(3)
I(2)-Bi(3)-I(4)#4	84.95(3)
I(3)-Bi(3)-I(4)#4	179.34(3)
I(1)-Bi(3)-I(4)#4	84.08(3)
I(4)-Bi(3)-I(4)#4	88.39(3)
I(2)-Bi(3)-I(1)#3	179.28(3)
I(3)-Bi(3)-I(1)#3	84.07(3)
I(1)-Bi(3)-I(1)#3	89.36(2)
I(4)-Bi(3)-I(1)#3	82.84(3)
I(4)#4-Bi(3)-I(1)#3	95.53(3)

Symmetry transformations used to generate equivalent atoms:

#1 x,-y,-z+1 #2 -x+1,y,-z+1/2 #3 x,-y,-z+2 #4 -x,y,-z+5/2

Table T2. Hydrogen bonds for 1 [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(1)-H(1A)...I(1)	0.89	3.35	4.182(9)	157.2
N(1)-H(1B)...I(4)#3	0.89	3.07	3.747(13)	133.8
N(1)-H(1C)...I(3)#5	0.89	2.98	3.765(2)	147.4
N(1)-H(1C)...I(4)#5	0.89	3.24	3.747(13)	118.8
N(2)-H(2B)...I(2)#6	0.89	3.01	3.7297(18)	139.5
N(2)-H(2C)...I(1)#7	0.89	3.07	3.752(12)	135.0
N(2)-H(2C)...I(2)#7	0.89	3.18	3.7297(18)	121.9
N(1)-H(1A)...I(1)	0.89	3.35	4.182(9)	157.2
N(1)-H(1B)...I(4)#3	0.89	3.07	3.747(13)	133.8
N(1)-H(1C)...I(3)#5	0.89	2.98	3.765(2)	147.4
N(1)-H(1C)...I(4)#5	0.89	3.24	3.747(13)	118.8
N(2)-H(2B)...I(2)#6	0.89	3.01	3.7297(18)	139.5
N(2)-H(2C)...I(1)#7	0.89	3.07	3.752(12)	135.0
N(2)-H(2C)...I(2)#7	0.89	3.18	3.7297(18)	121.9

Symmetry transformations used to generate equivalent atoms:

#1 x,-y,-z+1 #2 -x+1,y,-z+1/2 #3 x,-y,-z+2

#4 -x,y,-z+5/2 #5 x,y,z-1 #6 x+1/2,-y+1/2,-z+1

#7 -x+1/2,-y+1/2,z-1/2

Solid state structure and experimental details of 2

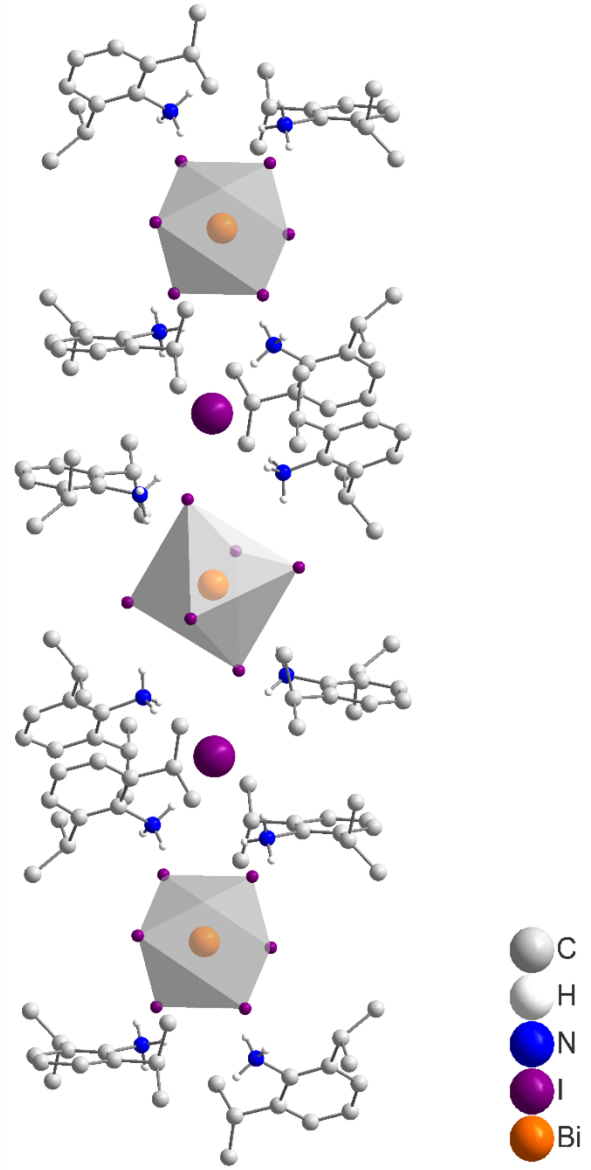

Figure S1: molecular structure of compound [2,6-diisopropylanilinium]$_4$[BiI$_6$][I] (**2**). Discrete [BiI$_6$] units have been presented as octahedrons.

Experimental details of compound 2: Compound **2** was obtained by following the same reaction procedure as **1**. An excess of HI (1.8 mmol) was added and the red coloured crystals were obtained from the methanol solution.

Yield 85% (according to bismuth). Elemental analysis calculated for $C_{48}H_{80}N_4BiI_7$ C 31.84, H 4.45, N 3.09 and found C = 31.46, H = 4.21, N= 3.15. IR analysis: 3062(m), 2960(s), 2872(s),2507(w), 1562(m), 1467(s), 1342(w), 1012(w), 794(m), 720(w).

Crystal data and structure refinement for 2.

Identification code	**2**
Empirical formula	$C_{48}H_{80}BiI_7N_4$
Formula weight	1810.44

Temperature	296(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	*C*2/c	
Unit cell dimensions	a = 18.372(3) Å	α= 90°.
	b = 18.431(2) Å	β= 101.319(9)°.
	c = 19.530(3) Å	γ = 90°.
Volume	6484.4(15) $Å^3$	
Z	4	
Density (calculated)	1.854 Mg/m^3	
Absorption coefficient	6.082 mm^{-1}	
F(000)	3400	
Crystal size	0.150 x 0.150 x 0.100 mm^3	
Theta range for data collection	2.823 to 25.999°.	
Index ranges	-22<=h<=22, -22<=k<=22, -23<=l<=24	
Reflections collected	24638	
Independent reflections	6234 [R(int) = 0.0489]	
Completeness to theta = 25.242°	97.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.581 and 0.462	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6234 / 1 / 283	
Goodness-of-fit on F^2	1.030	
Final R indices [I>2σ(I)]	R1 = 0.0418, wR2 = 0.0864	
R indices (all data)	R1 = 0.0922, wR2 = 0.1062	
Extinction coefficient	n/a	
Largest diff. peak and hole	1.063 and -1.163 e.$Å^{-3}$	

Table T3: Bond lengths [Å] and angles [°] for 2.

C(1)-C(6)	1.382(10)
C(1)-C(2)	1.386(11)
C(1)-N(1)	1.476(9)
C(2)-C(3)	1.379(11)
C(2)-C(7)	1.524(11)
C(3)-C(4)	1.377(13)
C(3)-H(3)	0.9300
C(4)-C(5)	1.353(13)
C(4)-H(4)	0.9300
C(5)-C(6)	1.394(11)
C(5)-H(5)	0.9300
C(6)-C(10)	1.532(13)
C(7)-C(8)	1.513(12)
C(7)-C(9)	1.539(13)
C(7)-H(7)	0.9800
C(8)-H(8A)	0.9600
C(8)-H(8B)	0.9600
C(8)-H(8C)	0.9600
C(9)-H(9A)	0.9600
C(9)-H(9B)	0.9600
C(9)-H(9C)	0.9600
C(10)-C(12)	1.454(16)
C(10)-C(11)	1.463(15)
C(10)-H(10)	0.9800
C(11)-H(11A)	0.9600
C(11)-H(11B)	0.9600
C(11)-H(11C)	0.9600
C(12)-H(12A)	0.9600
C(12)-H(12B)	0.9600
C(12)-H(12C)	0.9600
C(13)-C(18)	1.366(11)
C(13)-C(14)	1.419(11)
C(13)-N(2)	1.500(9)

C(14)-C(15)	1.390(12)
C(14)-C(19)	1.493(13)
C(15)-C(16)	1.365(13)
C(15)-H(15)	0.9300
C(16)-C(17)	1.360(12)
C(16)-H(16)	0.9300
C(17)-C(18)	1.371(11)
C(17)-H(17)	0.9300
C(18)-C(22)	1.514(11)
C(19)-C(20)	1.467(17)
C(19)-C(21)	1.550(19)
C(19)-H(19)	0.9800
C(20)-H(20A)	0.9600
C(20)-H(20B)	0.9600
C(20)-H(20C)	0.9600
C(21)-H(21A)	0.9600
C(21)-H(21B)	0.9600
C(21)-H(21C)	0.9600
C(22)-C(23)	1.521(13)
C(22)-C(24)	1.531(13)
C(22)-H(22)	0.9800
C(23)-H(23A)	0.9600
C(23)-H(23B)	0.9600
C(23)-H(23C)	0.9600
C(24)-H(24A)	0.9600
C(24)-H(24B)	0.9600
C(24)-H(24C)	0.9600
N(1)-H(1A)	0.8900
N(1)-H(1B)	0.8900
N(1)-H(1C)	0.8900
N(2)-H(2A)	0.8900
N(2)-H(2B)	0.8900
N(2)-H(2C)	0.8900
I(1)-Bi(1)	3.0913(6)
I(2)-Bi(1)	3.0700(6)
I(3)-Bi(1)	3.0798(6)

Bi(1)-I(2)#1	3.0701(6)
Bi(1)-I(3)#1	3.0798(6)
Bi(1)-I(1)#1	3.0913(6)

C(6)-C(1)-C(2)	124.6(7)
C(6)-C(1)-N(1)	117.7(7)
C(2)-C(1)-N(1)	117.6(7)
C(3)-C(2)-C(1)	116.2(8)
C(3)-C(2)-C(7)	120.4(8)
C(1)-C(2)-C(7)	123.4(7)
C(4)-C(3)-C(2)	121.5(9)
C(4)-C(3)-H(3)	119.3
C(2)-C(3)-H(3)	119.3
C(5)-C(4)-C(3)	119.9(9)
C(5)-C(4)-H(4)	120.0
C(3)-C(4)-H(4)	120.0
C(4)-C(5)-C(6)	122.1(9)
C(4)-C(5)-H(5)	118.9
C(6)-C(5)-H(5)	118.9
C(1)-C(6)-C(5)	115.5(8)
C(1)-C(6)-C(10)	122.8(8)
C(5)-C(6)-C(10)	121.6(8)
C(8)-C(7)-C(2)	110.5(7)
C(8)-C(7)-C(9)	111.0(8)
C(2)-C(7)-C(9)	110.6(8)
C(8)-C(7)-H(7)	108.2
C(2)-C(7)-H(7)	108.2
C(9)-C(7)-H(7)	108.2
C(7)-C(8)-H(8A)	109.5
C(7)-C(8)-H(8B)	109.5
H(8A)-C(8)-H(8B)	109.5
C(7)-C(8)-H(8C)	109.5
H(8A)-C(8)-H(8C)	109.5
H(8B)-C(8)-H(8C)	109.5
C(7)-C(9)-H(9A)	109.5
C(7)-C(9)-H(9B)	109.5

H(9A)-C(9)-H(9B)	109.5
C(7)-C(9)-H(9C)	109.5
H(9A)-C(9)-H(9C)	109.5
H(9B)-C(9)-H(9C)	109.5
C(12)-C(10)-C(11)	114.4(13)
C(12)-C(10)-C(6)	112.5(10)
C(11)-C(10)-C(6)	111.8(10)
C(12)-C(10)-H(10)	105.8
C(11)-C(10)-H(10)	105.8
C(6)-C(10)-H(10)	105.8
C(10)-C(11)-H(11A)	109.5
C(10)-C(11)-H(11B)	109.5
H(11A)-C(11)-H(11B)	109.5
C(10)-C(11)-H(11C)	109.5
H(11A)-C(11)-H(11C)	109.5
H(11B)-C(11)-H(11C)	109.5
C(10)-C(12)-H(12A)	109.5
C(10)-C(12)-H(12B)	109.5
H(12A)-C(12)-H(12B)	109.5
C(10)-C(12)-H(12C)	109.5
H(12A)-C(12)-H(12C)	109.5
H(12B)-C(12)-H(12C)	109.5
C(18)-C(13)-C(14)	124.5(8)
C(18)-C(13)-N(2)	119.6(7)
C(14)-C(13)-N(2)	115.9(7)
C(15)-C(14)-C(13)	114.4(8)
C(15)-C(14)-C(19)	122.5(8)
C(13)-C(14)-C(19)	123.1(8)
C(16)-C(15)-C(14)	122.5(9)
C(16)-C(15)-H(15)	118.8
C(14)-C(15)-H(15)	118.8
C(17)-C(16)-C(15)	119.6(9)
C(17)-C(16)-H(16)	120.2
C(15)-C(16)-H(16)	120.2
C(16)-C(17)-C(18)	122.5(9)
C(16)-C(17)-H(17)	118.8

C(18)-C(17)-H(17)	118.8
C(13)-C(18)-C(17)	116.6(8)
C(13)-C(18)-C(22)	122.4(8)
C(17)-C(18)-C(22)	120.9(8)
C(20)-C(19)-C(14)	114.3(12)
C(20)-C(19)-C(21)	109.4(13)
C(14)-C(19)-C(21)	109.0(10)
C(20)-C(19)-H(19)	108.0
C(14)-C(19)-H(19)	108.0
C(21)-C(19)-H(19)	108.0
C(19)-C(20)-H(20A)	109.5
C(19)-C(20)-H(20B)	109.5
H(20A)-C(20)-H(20B)	109.5
C(19)-C(20)-H(20C)	109.5
H(20A)-C(20)-H(20C)	109.5
H(20B)-C(20)-H(20C)	109.5
C(19)-C(21)-H(21A)	109.5
C(19)-C(21)-H(21B)	109.5
H(21A)-C(21)-H(21B)	109.5
C(19)-C(21)-H(21C)	109.5
H(21A)-C(21)-H(21C)	109.5
H(21B)-C(21)-H(21C)	109.5
C(18)-C(22)-C(23)	109.3(8)
C(18)-C(22)-C(24)	112.8(8)
C(23)-C(22)-C(24)	113.2(9)
C(18)-C(22)-H(22)	107.1
C(23)-C(22)-H(22)	107.1
C(24)-C(22)-H(22)	107.1
C(22)-C(23)-H(23A)	109.5
C(22)-C(23)-H(23B)	109.5
H(23A)-C(23)-H(23B)	109.5
C(22)-C(23)-H(23C)	109.5
H(23A)-C(23)-H(23C)	109.5
H(23B)-C(23)-H(23C)	109.5
C(22)-C(24)-H(24A)	109.5
C(22)-C(24)-H(24B)	109.5

H(24A)-C(24)-H(24B) 109.5

C(22)-C(24)-H(24C) 109.5

H(24A)-C(24)-H(24C) 109.5

H(24B)-C(24)-H(24C) 109.5

C(1)-N(1)-H(1A) 109.5

C(1)-N(1)-H(1B) 109.5

H(1A)-N(1)-H(1B) 109.5

C(1)-N(1)-H(1C) 109.5

H(1A)-N(1)-H(1C) 109.5

H(1B)-N(1)-H(1C) 109.5

C(13)-N(2)-H(2A) 109.5

C(13)-N(2)-H(2B) 109.5

H(2A)-N(2)-H(2B) 109.5

C(13)-N(2)-H(2C) 109.5

H(2A)-N(2)-H(2C) 109.5

H(2B)-N(2)-H(2C) 109.5

I(2)-Bi(1)-I(2)#1 180.0

I(2)-Bi(1)-I(3) 88.179(18)

I(2)#1-Bi(1)-I(3) 91.820(18)

I(2)-Bi(1)-I(3)#1 91.821(18)

I(2)#1-Bi(1)-I(3)#1 88.180(18)

I(3)-Bi(1)-I(3)#1 180.0

I(2)-Bi(1)-I(1)#1 90.518(17)

I(2)#1-Bi(1)-I(1)#1 89.482(17)

I(3)-Bi(1)-I(1)#1 92.67(2)

I(3)#1-Bi(1)-I(1)#1 87.327(19)

I(2)-Bi(1)-I(1) 89.482(17)

I(2)#1-Bi(1)-I(1) 90.518(17)

I(3)-Bi(1)-I(1) 87.33(2)

I(3)#1-Bi(1)-I(1) 92.67(2)

I(1)#1-Bi(1)-I(1) 180.0

Symmetry transformations used to generate equivalent atoms:

#1 -x-1/2,-y+3/2,-z+1

Table T4: Hydrogen bonds for 2 [Å and °].

D-H.....A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(1)-H(1A)...I(1)#1	0.89	3.07	3.706(6)	130.0
N(1)-H(1B)...I(4)	0.89	2.70	3.490(6)	148.8
N(1)-H(1C)...I(2)	0.89	2.95	3.599(6)	131.6
N(1)-H(1A)...I(3)	0.89	2.97	3.601(6)	129.2
N(2)-H(2A)...I(2)#2	0.89	2.79	3.548(6)	143.7
N(2)-H(2B)...I(4)	0.89	2.77	3.558(6)	148.4
N(2)-H(2C)...I(1)#3	0.89	3.10	3.677(6)	124.1
N(2)-H(2C)...I(3)#3	0.89	3.06	3.735(7)	133.8

Symmetry transformations used to generate equivalent atoms:

#1 -x-1/2,-y+3/2,-z+1 #2 -x,y,-z+3/2 #3 x+1/2,-y+3/2,z+1/2

Thermo gravimetry Analysis Plot of compound 1:

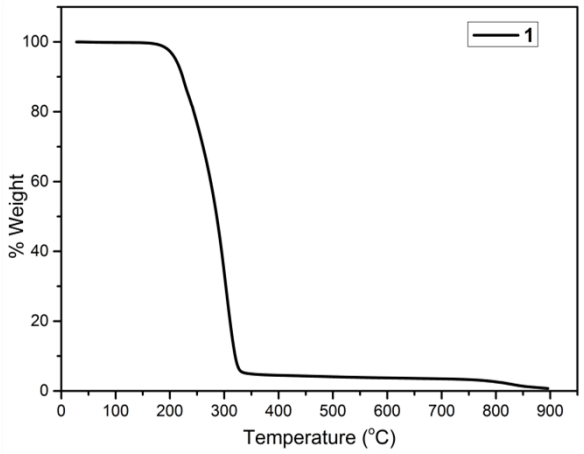

*Figure S2: TGA plot of **1***

Table T5: Bond lengths [Å] of 1 at 85 K and 296K

Inter-atomic distances	298 K (Å)	85K (Å)	Change upon cooling (Å)
I----I			
I2---I2’’’	4.315	4.319	0.004
I1’’---I2’	3.962	3.958	0.004
I1’---I4	4.261	4.268	0.007
I4’---I4’’	4.945	4.969	0.026
Bi---Bi			
Bi1----Bi2	4.583	4.588	0.005
Bi2---Bi3	4.631	4.638	0.007
Bi–I			
Bi1–I1(bridged)	3.381	3.384	0.003
Bi1–I2(bridged)	3.063	3.069	0.006
Bi1–I3(terminal)	2.882	2.890	0.008
Bi1–I4(terminal)	2.894	2.903	0.009
Bi1–I’(bridged)	3.077	3.083	0.006
Bi1–I2’(bridged)	3.383	3.387	0.004
N---I			
N2---I2’	4.159	4.144	−0.015
N2---I1’	3.717	3.706	−0.011
N1---I2’’	3.756	3.781	0.025
N1---I3’	3.723	3.721	−0.002
N1---I1’	4.210	4.220	0.010

‘–‘ signs denotes the decrease in the inter atomic distances upon cooling.

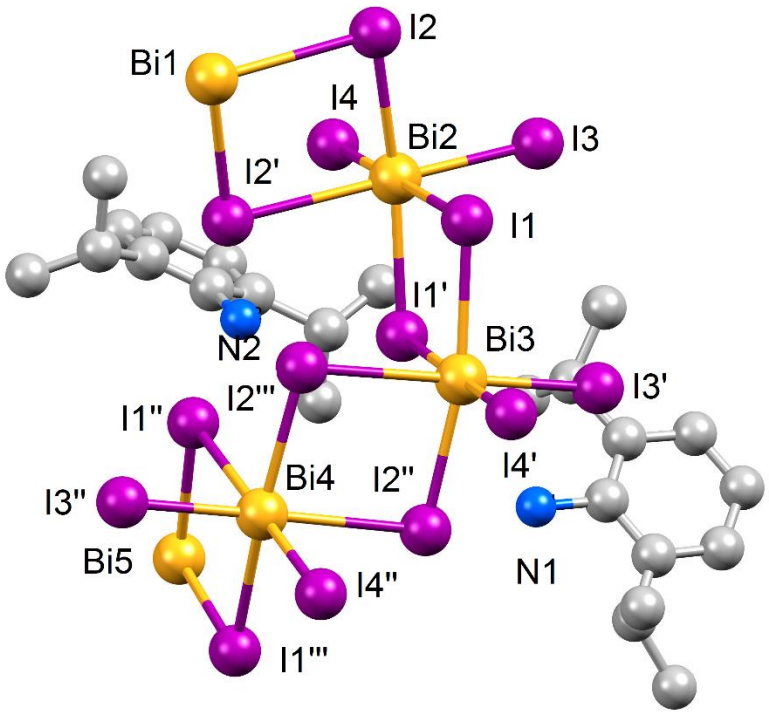

*Figure S3: Atom labels for compound **1.***

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