α- to β-(*dmes*)BiI_5 (*dmes* = dimethyl(2-ethylammonium)sulfonium dication): Umbrella Reversal of Sulfonium in Solid State, and Short I…I Interchain Contacts: Crystal Structures, Optical Properties and Theoretical Investigations of 1D iodobismuthates.

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Supporting Information

I- $(HO_2C(C_6H_4)CH_2NH_3)BiI_4$ (compound 3)

I-A- Checkcif

Bond precision: C-C = 0.0129 A Wavelength=0.71073
Cell: a=8.1071(16) b=9.871(2) c=12.271(3)
alpha=68.97(3) beta=83.37(3) gamma=83.48(3)

	Calculated	Reported
Volume	907.7(4)	907.7(3)
Space group	P -1	P -1
Hall group	-P 1	?
Moiety formula	C8 H15 N O2, Bi I4	?
Sum formula	C8 H15 Bi I4 N O2	C8 H15 Bi I4 N O2
Mr	873.79	873.79
Dx,g cm-3	3.197	3.197
Z	2	2
Mu (mm-1)	16.505	16.505
F000	762.0	762.0
F000'	750.81	
h,k,lmax	11,13,17	11,13,17
Nref	5301	5280
Tmin,Tmax	0.150,0.438	0.141,0.463
Tmin'	0.040	

Correction method= AbsCorr=MULTI-SCAN
Data completeness= Ratio = 0.996 Theta(max)= 30.020
R(reflections)= 0.0411(3632) wR2(reflections)= 0.0924(5280)
S = 1.036 Npar= 146

Alert level A

PLAT761_ALERT_1_A CIF Contains no X-H Bonds ..... ?
PLAT762_ALERT_1_A CIF Contains no X-Y-H or H-Y-H Angles ... ?

Alert level C

ABSTY02_ALERT_1_C An _exptl_absorpt_correction_type has been given without a literature citation. This should be contained in the _exptl_absorpt_process_details field.
Absorption correction given as multi-scan
PLAT048_ALERT_1_C MoietyFormula Not Given ..... ?
PLAT062_ALERT_4_C Rescale T(min) & T(max) by 0.95
PLAT125_ALERT_4_C No _symmetry_space_group_name_Hall Given .. ?
PLAT152_ALERT_1_C Supplied and Calc Volume s.u. Inconsistent .. ?
PLAT154_ALERT_1_C The su's on the Cell Angles are Equal (x 10000) 3000 eg.

PLAT242_ALERT_2_C Check Low Ueq as Compared to Neighbors for Bi
PLAT250_ALERT_2_C Large U3/U1 Ratio for Average U(i,j) Tensor .. 2.12
PLAT342_ALERT_3_C Low Bond Precision on C-C Bonds (x 1000) Ang .. 13
PLAT420_ALERT_2_C D-H Without Acceptor N - H1B ?
PLAT764_ALERT_4_C Overcomplete CIF Bond List Detected (Rep/Expd) . 1.12 Ratio

I-B- Summary of crystallographic data

Empirical formula	C8 H15 Bi I4 N O2
Formula weight	873.79
Temperature	293(2) K
Wavelength	0.71073 A
Crystal system, space group	triclinic, P-1
Unit cell dimensions	a = 8.1071(16) A alpha = 68.97(3) deg.
	b = 9.871(2) A beta = 83.37(3) deg.
	c = 12.271(3) A gamma = 83.48(3) deg.
Volume	907.7(3) A^3
Z, Calculated density	2, 3.197 Mg/m^3
Absorption coefficient	16.505 mm^-1
F(000)	762
Crystal size	0.20 x 0.10 x 0.05 mm
Theta range for data collection	3.48 to 30.02 deg.
Limiting indices	-11<=h<=11, -13<=k<=13, -17<=l<=17
Reflections collected / unique	22988 / 5280 [R(int) = 0.0484]
Completeness to theta = 30.02	99.6 %
Absorption correction	None
Max. and min. transmission	0.1369 and 0.0831
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5280 / 0 / 146
Goodness-of-fit on F^2	1.036
Final R indices [I>2sigma(I)]	R1 = 0.0411, wR2 = 0.0835
R indices (all data)	R1 = 0.0788, wR2 = 0.0924
Largest diff. peak and hole	1.580 and -2.519 e.A^-3

I-C- Tables

Table 1. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for 3.
U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
Bi	2465(1)	6196(1)	4251(1)	35(1)
I(1)	1417(1)	7554(1)	1871(1)	65(1)
I(2)	1045(1)	3194(1)	4464(1)	49(1)
I(3)	6004(1)	5815(1)	3241(1)	44(1)
I(4)	3058(1)	9010(1)	4441(1)	56(1)
O(1)	297(7)	3362(7)	1032(5)	56(2)
O(2)	2167(7)	4808(8)	-117(6)	73(2)
N	9089(9)	793(8)	2859(7)	57(2)
C(1)	1752(10)	3638(9)	735(8)	45(2)
C(2)	3181(10)	2616(9)	1329(8)	44(2)
C(3)	4055(11)	1824(11)	562(9)	57(2)
C(4)	4398(9)	3434(8)	1675(8)	40(2)
C(5)	5419(10)	725(10)	1209(9)	51(2)
C(6)	5751(9)	2351(9)	2357(7)	40(2)
C(7)	6645(9)	1436(9)	1674(8)	45(2)
C(8)	7858(11)	242(10)	2385(10)	59(3)

Table 2. Selected bond distances (Å) and angles (°) for **3**.

Bi-I(1)	2.9241(12)	Bi-I(2)#1	3.1947(11)
Bi-I(4)	2.9663(9)	Bi-I(2)	3.2130(10)
Bi-I(3)	3.0294(10)	Bi-I(3)#2	3.2999(14)
O(1)-C(1)	1.226(10)	C(3)-C(5)	1.530(12)
O(2)-C(1)	1.296(10)	C(4)-C(6)	1.533(10)
N-C(8)	1.454(11)	C(5)-C(7)	1.543(11)
C(1)-C(2)	1.514(10)	C(6)-C(7)	1.516(11)
C(2)-C(3)	1.500(12)	C(7)-C(8)	1.521(11)
C(2)-C(4)	1.526(11)		
O(1)-C(1)-O(2)	122.3(7)	N-C(8)-C(7)	113.1(7)
O(1)-C(1)-C(2)	121.9(7)	O(2)-C(1)-C(2)	115.8(7)
Bi#1-I(2)-Bi	94.83(3)	Bi-I(3)-Bi#2	96.33(4)

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

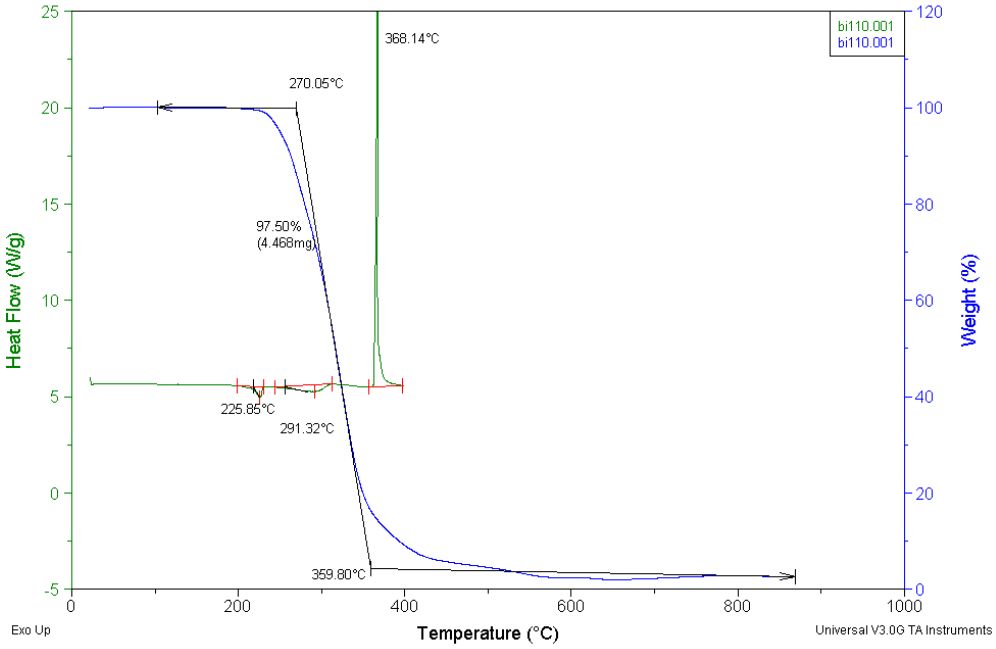
Table 3. Anisotropic displacement parameters (A^2 x 10^3) for 3.
The anisotropic displacement factor exponent takes the form:
-2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
Bi	34(1)	31(1)	39(1)	-12(1)	-3(1)	1(1)
I(1)	63(1)	82(1)	43(1)	-21(1)	-12(1)	27(1)
I(2)	44(1)	46(1)	65(1)	-31(1)	10(1)	-8(1)
I(3)	37(1)	50(1)	41(1)	-14(1)	-1(1)	1(1)
I(4)	71(1)	42(1)	56(1)	-14(1)	0(1)	-13(1)
O(1)	29(3)	62(4)	59(4)	4(3)	-10(3)	-10(3)
O(2)	31(3)	74(5)	79(5)	16(4)	-5(3)	-7(3)
N	37(4)	52(4)	62(5)	6(4)	-16(4)	0(3)
C(1)	38(4)	41(4)	48(5)	-6(4)	-16(4)	4(4)
C(2)	33(4)	50(5)	47(5)	-13(4)	-11(4)	0(3)
C(3)	52(5)	70(6)	67(7)	-45(5)	-18(5)	9(5)
C(4)	33(4)	34(4)	53(5)	-17(4)	-10(4)	8(3)
C(5)	39(4)	54(5)	72(6)	-40(5)	-7(4)	2(4)
C(6)	30(4)	44(4)	48(5)	-18(4)	-10(4)	0(3)
C(7)	29(4)	52(5)	56(5)	-23(4)	-5(4)	8(3)
C(8)	41(5)	41(5)	85(7)	-14(5)	-14(5)	18(4)

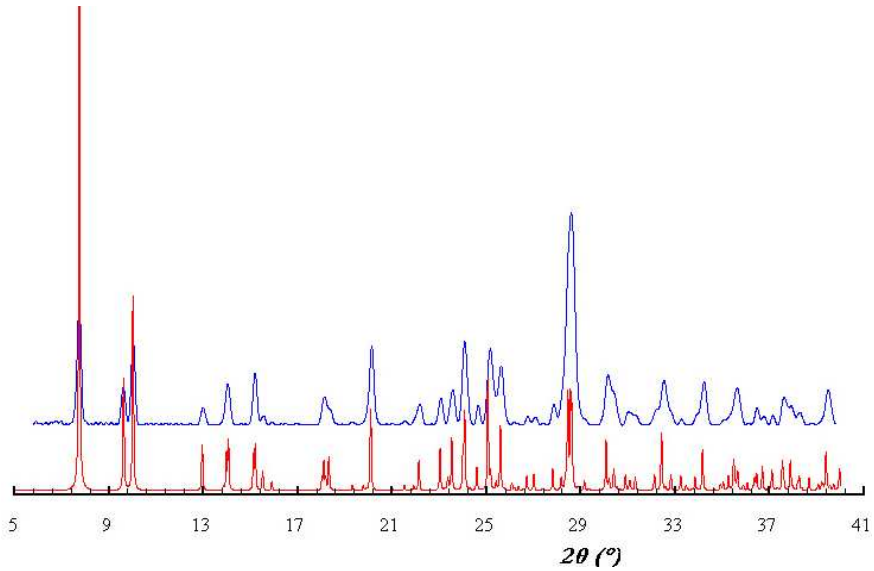
Table 4 - Hydrogen bonds with H..A < r(A) + 2.000 Angstroms and <DHA > 110 deg.

D-H	d(D-H)	d(H..A)	<DHA	d(D..A)	A
N-H1A	0.890	2.008	177.32	2.897	O1 [x+1, y, z]
N-H1B	0.890	3.073	149.02	3.863	I4 [x+1, y-1, z]
N-H1C	0.890	2.755	164.16	3.619	I4 [-x+1, -y+1, -z+1]

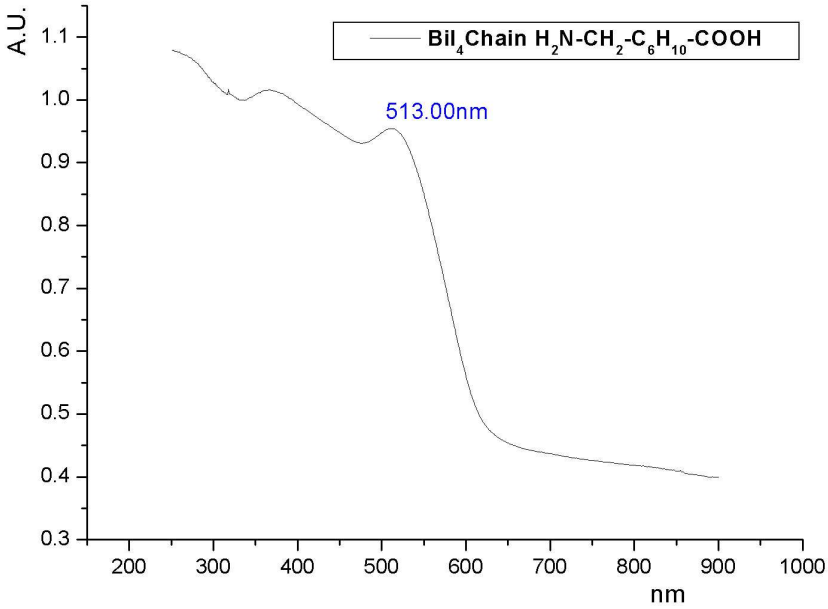
I-C- TGA-DSC



I-E- XRPD: theor



I-F- UV-VIS spectrum of 3



II- (*dmes*)SbI_5 (compound 2)

II-A- Checkcif

```
Bond precision:     C-C = 0.0120 A              Wavelength=0.71073
Cell:  a=8.4951(10)     b=12.8193(15)  c=15.694(2)
       alpha=90         beta=90        gamma=90
```

	Calculated	Reported
Volume	1709.1(4)	1709.1(4)
Space group	P 21 21 21	P 21 21 21
Hall group	P 2ac 2ab	?
Moiety formula	C4 H13 N S, I5 Sb	?
Sum formula	C4 H13 I5 N S Sb	C4 H13 I5 N S Sb
Mr	863.48	863.46
Dx,g cm-3	3.356	3.356
Z	4	4
Mu (mm-1)	10.737	10.737
F000	1504.0	1504.0
F000'	1493.33	
h,k,lmax	11,18,22	11,17,22
Nref	2824(4987)	4944
Tmin,Tmax	0.326,0.472	0.270,0.432
Tmin'	0.187	

```
Correction method= AbsCorr=MULTI-SCAN
Data completeness= 1.75(0.99)   Theta(max)= 30.010
R(reflections)= 0.0315( 3906)      wR2(reflections)= 0.0578( 4944)
S = 1.028             Npar= 109
```

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level A

PLAT761_ALERT_1_A CIF Contains no X-H Bonds ..... ?
PLAT762_ALERT_1_A CIF Contains no X-Y-H or H-Y-H Angles .....

Alert level C

ABSTY02_ALERT_1_C An _exptl_absorpt_correction_type has been given without a literature citation. This should be contained in the _exptl_absorpt_process_details field. Absorption correction given as multi-scan
PLAT048_ALERT_1_C MoietyFormula Not Given ..... ?
PLAT062_ALERT_4_C Rescale T(min) & T(max) by 1.09
PLAT125_ALERT_4_C No _symmetry_space_group_name_Hall Given .. ?
PLAT242_ALERT_2_C Check Low Ueq as Compared to Neighbors for Sb
PLAT342_ALERT_3_C Low Bond Precision on C-C Bonds (x 1000) Ang .. 12
PLAT420_ALERT_2_C D-H Without Acceptor N - H00B ?
PLAT720_ALERT_4_C Number of Unusual/Non-Standard Label(s) . 13
PLAT850_ALERT_2_C Check Flack Parameter Exact Value 0.00 and su .. 0.06

II-B- Summary of crystallographic data

Empirical formula	C4 H13 I5 N S Sb
Formula weight	863.46
Temperature	293(2) K
Wavelength	0.71073 A
Crystal system, space group	orthorhombic, P 21 21 21
Unit cell dimensions	a = 8.4951(10) A alpha = 90 deg. b = 12.8193(15) A beta = 90 deg. c = 15.694(2) A gamma = 90 deg.
Volume	1709.1(4) A^3
Z, Calculated density	4, 3.356 Mg/m^3
Absorption coefficient	10.737 mm^-1
F(000)	1504
Crystal size	0.16 x 0.09 x 0.07 mm
Theta range for data collection	3.88 to 30.01 deg.
Limiting indices	-11<=h<=11, -12<=k<=17, -20<=l<=22
Reflections collected / unique	24196 / 4944 [R(int) = 0.0338]
Completeness to theta = 30.01	99.4 %
Absorption correction	None
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4944 / 0 / 109
Goodness-of-fit on F^2	1.028
Final R indices [I>2sigma(I)]	R1 = 0.0315, wR2 = 0.0523
R indices (all data)	R1 = 0.0543, wR2 = 0.0578
Absolute structure parameter	0.00(6)
Largest diff. peak and hole	1.792 and -1.529 e.A^-3

II-C- Tables

Table 1. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for 2.
U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
Sb	12339(1)	11042(1)	-4113(1)	28(1)
I(2)	9464(1)	12318(1)	-4816(1)	49(1)
I(3)	12560(1)	12505(1)	-2610(1)	40(1)
I(4)	12220(1)	9719(1)	-5692(1)	51(1)
I(5)	15084(1)	9919(1)	-3487(1)	51(1)
I(1)	10263(1)	9677(1)	-3235(1)	51(1)
S	8203(3)	11468(2)	-908(2)	69(1)
N	6749(8)	12850(6)	-3080(4)	65(2)
C(4)	7887(12)	10111(7)	-1022(7)	77(3)
C(1)	7671(9)	12200(6)	-2506(5)	55(2)
C(2)	6927(9)	12104(8)	-1656(6)	70(3)
C(3)	7067(15)	11726(10)	31(6)	102(4)

Symmetry transformations used to generate equivalent atoms:

Table 2. Selected bond distances (Å) and angles (°) for **2**.

Sb-I(1)	2.8406(6)	Sb-I(3)	3.0196(6)
Sb-I(5)	2.9111(6)	Sb-I(2)	3.1394(6)
Sb-I(4)	3.0036(7)	Sb-I(2)#1	3.2410(5)
S-C(4)	1.770(9)	N-C(1)	1.456(10)
S-C(3)	1.792(11)	C(1)-C(2)	1.481(11)
S-C(2)	1.795(8)		
C(4)-S-C(3)	100.5(6)	C(1)-C(2)-S	111.7(6)
C(4)-S-C(2)	106.8(5)	N-C(1)-C(2)	112.0(7)
C(3)-S-C(2)	97.4(5)	I(2)-Sb-I(2)#1	162.47(2)

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

Table 3. Anisotropic displacement parameters (A^2 x 10^3) for 3.
The anisotropic displacement factor exponent takes the form:
-2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

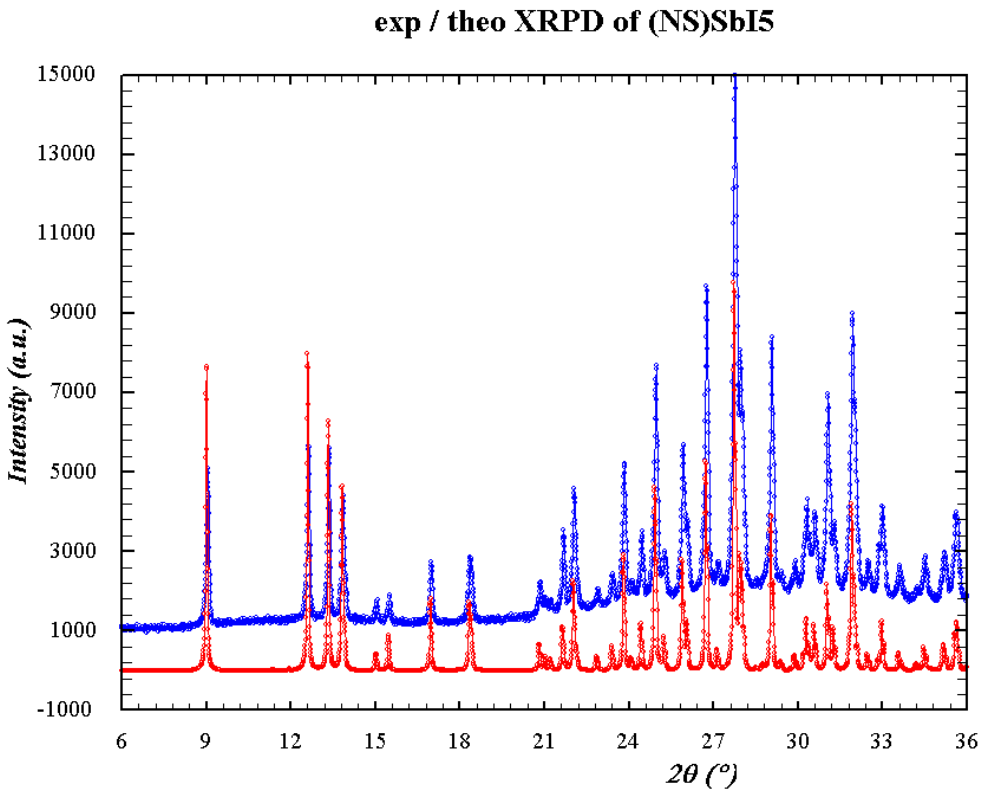
	U11	U22	U33	U23	U13	U12
Sb	27(1)	25(1)	32(1)	6(1)	3(1)	2(1)
I(2)	39(1)	63(1)	44(1)	12(1)	-3(1)	22(1)
I(3)	43(1)	42(1)	37(1)	-10(1)	-1(1)	4(1)
I(4)	61(1)	45(1)	48(1)	-16(1)	7(1)	-2(1)
I(5)	36(1)	49(1)	68(1)	12(1)	-5(1)	15(1)
I(1)	47(1)	41(1)	67(1)	15(1)	18(1)	-8(1)
S	55(1)	63(2)	89(2)	26(1)	-26(1)	-9(1)
N	64(4)	78(5)	52(4)	20(4)	20(3)	17(4)
C(4)	88(7)	41(5)	103(8)	3(5)	9(6)	2(5)
C(1)	46(4)	59(5)	59(5)	-7(4)	8(4)	-4(4)
C(2)	43(4)	90(7)	77(6)	25(5)	-3(4)	11(4)
C(3)	129(11)	100(8)	76(7)	-28(7)	-9(7)	31(8)

Table 4 - Hydrogen bonds with H..A < r(A) + 2.000 Angstroms and <DHA > 110 deg.

D-H	d(D-H)	d(H..A)	<DHA	d(D..A)	A
N-H00A	0.890	2.806	155.44	3.634	I2
N-H00B	0.890	3.182	144.16	3.938	I5 [-x+2, y+1/2, -z-1/2]
N-H00B	0.890	3.251	112.65	3.686	I4 [x-1/2, -y+5/2, -z-1]

N-H00C	0.890	2.863	149.94	3.661	I3 [x-1, y, z]

II-D- XRPD: theoretical (red) and experimental (blue)



III- α-(*dmes*)BiI_5 (compound 1a)

III-A- Checkcif

```
Bond precision:     C-C = 0.0160 A              Wavelength=0.71073
Cell:  a=8.4752(3)      b=12.6137(15)  c=16.385(2)
       alpha=90         beta=90        gamma=90
```

	Calculated	Reported
Volume	1751.6(3)	1751.6(3)
Space group	P21cn	P 21 c n
Hall group	P -2n 2a	P -2n 2a
Moiety formula	C4 H13 N S, Bi I5	?
Sum formula	C4 H13 Bi I5 N S	C4 H13 Bi I5 N S
Mr	950.70	950.69
Dx,g cm-3	3.605	3.605
Z	4	4
Mu (mm-1)	18.967	18.967
F000	1632.0	1632.0
F000'	1608.34	
h,k,lmax	11,17,23	11,17,23
Nref	2718(5114)	4664
Tmin,Tmax	0.291,0.366	0.228,0.440
Tmin'	0.003	

```
Correction method= AbsCorr=MULTI-SCAN
Data completeness= 1.72(0.91)   Theta(max)= 30.020
R(reflections)= 0.0333( 3247)      wR2(reflections)= 0.0604( 4664)
S = 0.977             Npar= 110
```

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level C

ABSTY02_ALERT_1_C An _exptl_absorpt_correction_type has been given without a literature citation. This should be contained in the _exptl_absorpt_process_details field.
Absorption correction given as multi-scan
PLAT048_ALERT_1_C MoietyFormula Not Given ..... ?
PLAT062_ALERT_4_C Rescale T(min) & T(max) by .....
PLAT128_ALERT_4_C Non-standard setting of Space group Pna21 P21cn
PLAT147_ALERT_1_C su on Symmetry Constrained Cell Angle(s) ... ?
PLAT242_ALERT_2_C Check Low Ueq as Compared to Neighbors for S
PLAT242_ALERT_2_C Check Low Ueq as Compared to Neighbors for Bi
PLAT342_ALERT_3_C Low Bond Precision on C-C Bonds (x 1000) Ang .. 16
PLAT420_ALERT_2_C D-H Without Acceptor N - H1E ?
PLAT480_ALERT_4_C Long H...A H-Bond Reported H1E .. I4 3.07 Ang.

III-B- Summary of crystallographic data

Empirical formula	C4 H13 Bi I5 N S
Formula weight	950.69
Temperature	293(2) K
Wavelength	0.71073 A
Crystal system, space group	orthorhombic, P 21 c n
Unit cell dimensions	a = 8.4752(3) A alpha = 90.000(11) deg. b = 12.6137(15) A beta = 90.000(7) deg. c = 16.385(2) A gamma = 90.000(7) deg.
Volume	1751.6(3) A^3
Z, Calculated density	4, 3.605 Mg/m^3
Absorption coefficient	18.967 mm^-1
F(000)	1632
Crystal size	0.3 x 0.05 x 0.05 mm
Theta range for data collection	3.15 to 30.02 deg.
Limiting indices	-9<=h<=11, -17<=k<=17, -22<=l<=23
Reflections collected / unique	34672 / 4664 [R(int) = 0.0784]
Completeness to theta = 30.02	99.6 %
Absorption correction	multi-scan
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4664 / 1 / 110
Goodness-of-fit on F^2	0.977
Final R indices [I>2sigma(I)]	R1 = 0.0333, wR2 = 0.0533
R indices (all data)	R1 = 0.0765, wR2 = 0.0604
Absolute structure parameter	0.256(5)
Largest diff. peak and hole	1.264 and -1.333 e.A^-3

III-C- Tables

Table 1. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for 1a.
U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
Bi	7950(1)	3413(1)	4230(1)	28(1)
I(3)	8131(1)	4814(1)	2695(1)	38(1)
I(2)	10835(1)	2259(1)	3705(1)	49(1)
I(4)	4980(1)	4758(1)	4862(1)	46(1)
I(1)	5689(1)	1895(1)	3519(1)	43(1)
I(5)	7875(1)	2239(1)	5862(1)	52(1)
S	7291(3)	6139(2)	8636(2)	59(1)
C(2)	8683(12)	5971(9)	7824(6)	63(3)
C(3)	8337(16)	5519(8)	9498(6)	75(4)
C(4)	7609(18)	7521(8)	8871(7)	91(5)
N	7238(9)	4831(6)	6825(5)	48(2)
C(1)	8534(12)	4939(9)	7399(6)	60(3)

Table 2. Selected bond distances (Å) and angles (°) for **1a.**

Bi-I(1)	2.9484(7)	Bi-I(3)	3.0774(7)
Bi-I(2)	2.9717(8)	Bi-I(4)	3.2077(7)
Bi-I(5)	3.0576(7)	Bi-I(4)#1	3.2405(7)
S-C(2)	1.790(10)	C(2)-C(1)	1.481(14)
S-C(4)	1.806(10)	N-C(1)	1.453(11)
S-C(3)	1.842(11)		
C(2)-S-C(4)	100.1(6)	N-C(1)-C(2)	116.8(9)
C(2)-S-C(3)	101.7(6)	C(1)-C(2)-S	113.4(8)
C(4)-S-C(3)	100.1(6)	Bi-I(4)-Bi#2	160.33(3)

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

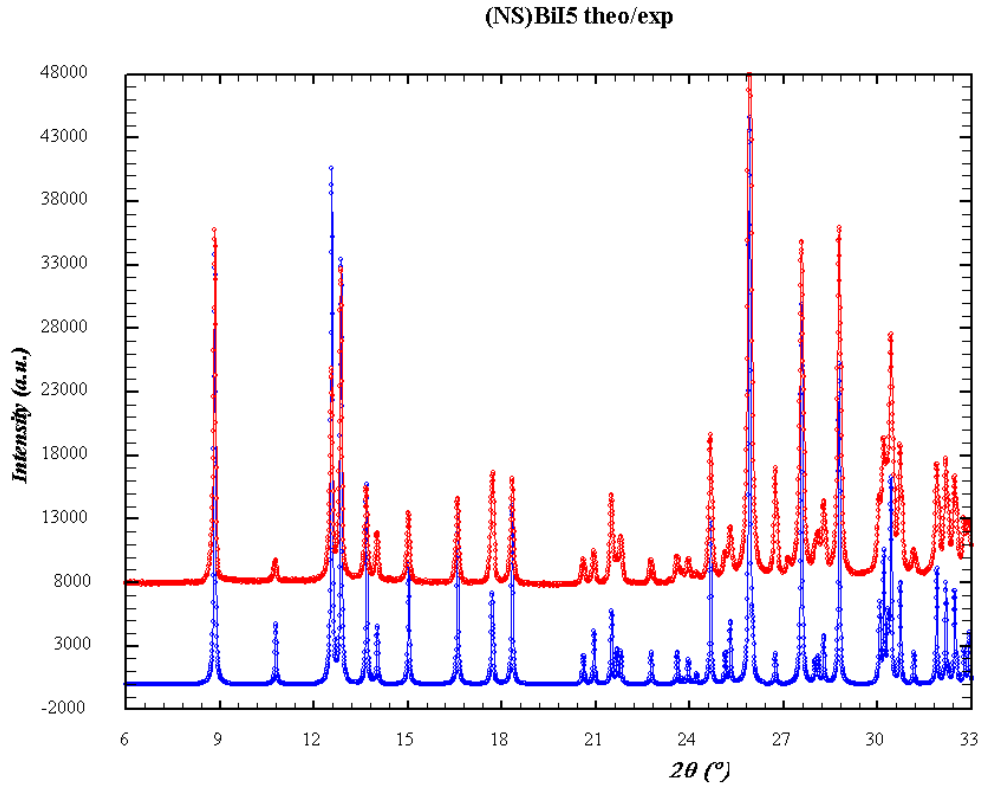
Table 3. Anisotropic displacement parameters (A^2 x 10^3) for 1a.
The anisotropic displacement factor exponent takes the form:
-2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
Bi	26(1)	26(1)	32(1)	-3(1)	1(1)	0(1)
I(3)	36(1)	45(1)	34(1)	6(1)	-1(1)	-6(1)
I(2)	32(1)	49(1)	66(1)	-8(1)	7(1)	11(1)
I(4)	42(1)	57(1)	39(1)	-11(1)	1(1)	23(1)
I(1)	33(1)	39(1)	57(1)	-13(1)	-3(1)	-7(1)
I(5)	63(1)	49(1)	43(1)	15(1)	0(1)	1(1)
S	51(2)	57(2)	69(2)	-9(1)	9(1)	-6(1)
C(2)	54(7)	80(9)	54(7)	-12(6)	1(5)	-21(6)
C(3)	127(13)	46(7)	51(6)	-1(5)	-1(7)	-1(8)
C(4)	101(12)	40(7)	131(12)	-35(7)	38(10)	-5(7)
N	35(4)	69(6)	38(5)	1(4)	-5(4)	-2(4)
C(1)	43(7)	94(9)	43(6)	-5(6)	-8(5)	-6(6)

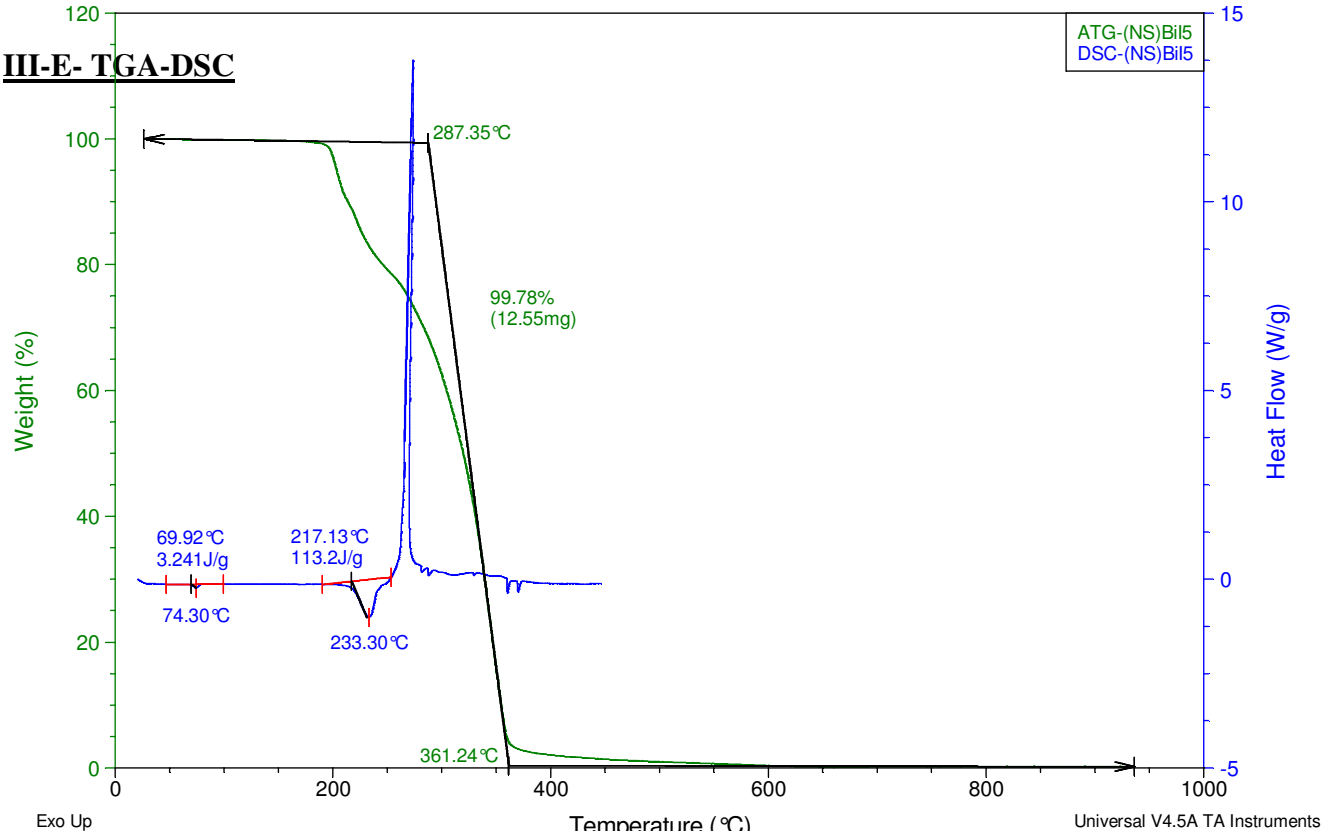
Table 4- Hydrogen bonds with H..A < r(A) + 2.000 Angstroms and <DHA > 110 deg.

D-H	d(D-H)	d(H..A)	<DHA	d(D..A)	A
N-H1C	0.890	2.793	168.62	3.670	I5
N-H1E	0.890	3.072	124.33	3.648	I4 [x+1/2, -y+1, -z+1
N-H1E	0.890	3.327	111.29	3.744	I4
N-H1D	0.890	2.752	159.06	3.597	I3 [x-1/2, -y+1, -z+1

III-D- XRPD: theoretical (blue) and experimental (red)



III-E- TGA-DSC



IV- β-(*dmes*)BiI_5 (compound 1b)

IV-A- Checkcif

Bond precision: C-C = 0.0200 A Wavelength=0.71073

Cell: a=8.5334(2) b=12.7319(10) c=16.195(2)
alpha=90 beta=90 gamma=90

Temperature: 293 K

	Calculated	Reported
Volume	1759.5(3)	1759.5(3)
Space group	P 21 21 21	P 21 21 21
Hall group	P 2ac 2ab	P 2ac 2ab
Moiety formula	C4 H13 N S, Bi I5	?
Sum formula	C4 H13 Bi I5 N S	C4 H13 Bi I5 N S
Mr	950.70	950.69
Dx,g cm-3	3.589	3.589
Z	4	4
Mu (mm-1)	18.882	18.881
F000	1632.0	1632.0
F000'	1608.34	
h,k,lmax	11,16,21	10,16,20
Nref	2310[4044]	3849
Tmin,Tmax	0.335,0.389	0.272,0.411
Tmin'	0.009	

Correction method= AbsCorr=MULTI-SCAN

Data completeness= 1.67[0.95] Theta(max)= 27.530

R(reflections)= 0.0310(3113) wR2(reflections)= 0.0446(3849)

S = 1.051 Npar= 110

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level A

PLAT241_ALERT_2_A Check High Ueq as Compared to Neighbors for C2
PLAT093_ALERT_1_A No su's on H-atoms, but refinement reported as . mixed
PLAT761_ALERT_1_A CIF Contains no X-H Bonds ..... ?
PLAT762_ALERT_1_A CIF Contains no X-Y-H or H-Y-H Angles .....

Alert level B

PLAT232_ALERT_2_B Hirshfeld Test Diff (M-X) Bi -- I5 12.33 su
PLAT242_ALERT_2_B Check Low Ueq as Compared to Neighbors for S
PLAT242_ALERT_2_B Check Low Ueq as Compared to Neighbors for C1

Alert level C

ABSTY02_ALERT_1_C An _exptl_absorpt_correction_type has been given without a literature citation. This should be contained in the

```
            _exptl_absorpt_process_details field.
            Absorption correction given as multi-scan
STRVA01_ALERT_4_C           Flack test results are ambiguous.
           From the CIF: _refine_ls_abs_structure_Flack    0.476
           From the CIF: _refine_ls_abs_structure_Flack_su    0.005
PLAT232_ALERT_2_C Hirshfeld Test Diff (M-X)  Bi     --  I3        9.13 su
PLAT232_ALERT_2_C Hirshfeld Test Diff (M-X)  Bi     --  I4       8.81 su
PLAT242_ALERT_2_C Check Low       Ueq as Compared to Neighbors for
Bi
PLAT342_ALERT_3_C Low Bond Precision on C-C Bonds (x 1000) Ang       20
PLAT360_ALERT_2_C Short  C(sp3)-C(sp3) Bond  C1     -   C2       1.41 Ang.
PLAT420_ALERT_2_C D-H Without Acceptor       N      -   H0B    .?
PLAT420_ALERT_2_C D-H Without Acceptor       N      -   H0C       ?
PLAT033_ALERT_4_C Flack Parameter Value Deviates from Zero ..     0.48
PLAT048_ALERT_1_C MoietyFormula Not Given ...............          ?
PLAT062_ALERT_4_C Rescale T(min) & T(max) by ............       0.95
PLAT194_ALERT_1_C Missing _cell_measurement_reflns_used datum           ?
PLAT195_ALERT_1_C Missing _cell_measurement_theta_max   datum          ?
PLAT196_ALERT_1_C Missing _cell_measurement_theta_min   datum          ?
PLAT720_ALERT_4_C Number of Unusual/Non-Standard Labels ....          3
```

IV-B- Summary of crystallographic data

Empirical formula	C4 H13 Bi I5 N S
Formula weight	950.69
Temperature	353(2) K
Wavelength	0.71073 A
Crystal system, space group	orthorhombic, P 21 21 21
Unit cell dimensions	a = 8.5334(2) A alpha = 90 deg. b = 12.7319(10) A beta = 90 deg. c = 16.195(2) A gamma = 90 deg.
Volume	1759.5(3) A^3
Z, Calculated density	4, 3.589 Mg/m^3
Absorption coefficient	18.881 mm^-1
F(000)	1632
Crystal size	0.25 x 0.05 x 0.05 mm
Theta range for data collection	2.70 to 27.53 deg.
Limiting indices	-10<=h<=10, -12<=k<=16, -20<=l<=20
Reflections collected / unique	19568 / 3849 [R(int) = 0.0382]
Completeness to theta = 27.53	99.2 %
Absorption correction	None
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3849 / 0 / 110
Goodness-of-fit on F^2	1.051
Final R indices [I>2sigma(I)]	R1 = 0.0310, wR2 = 0.0396
R indices (all data)	R1 = 0.0503, wR2 = 0.0446
Absolute structure parameter	0.476(5)
Largest diff. peak and hole	0.699 and -0.681 e.A^-3

IV-C- Tables

Table 1. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for 1b.
U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
Bi	7266(1)	10952(1)	4175(1)	39(1)
I(2)	10020(1)	9728(1)	3589(1)	69(1)
I(3)	7138(1)	9731(1)	5802(1)	73(1)
I(5)	7529(1)	12403(1)	2668(1)	56(1)
I(4)	4449(1)	12363(1)	4833(1)	70(1)
I(1)	5009(1)	9560(1)	3388(1)	79(1)
S	6646(4)	6357(3)	3860(2)	107(1)
C(1)	7413(14)	7266(10)	2431(7)	95(4)
N	8412(10)	7718(8)	1835(6)	99(3)
C(4)	7127(18)	5013(8)	3966(8)	122(5)
C(3)	7650(20)	6886(12)	4692(9)	180(8)
C(2)	8052(14)	6735(14)	3120(10)	152(7)

Table 2. Selected bond distances (Å) and angles (°) for **1b.**

Bi-I(1)	2.9111(7)	Bi-I(5)	3.0687(7)
Bi-I(2)	2.9744(7)	Bi-I(4)	3.1851(7)
Bi-I(3)	3.0623(8)	Bi-I(4)#1	3.2640(7)
S-C(2)	1.762(12)	C(2)-C(1)	1.414(15)
S-C(4)	1.768(11)	N-C(1)	1.411(12)
S-C(3)	1.735(15)		
C(2)-S-C(4)	99.9(7)	N-C(1)-C(2)	120.1(11)
C(2)-S-C(3)	94.8(9)	C(1)-C(2)-S	113.8(9)
C(4)-S-C(3)	100.6(8)	Bi-I(4)-Bi#2	165.08(2)

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

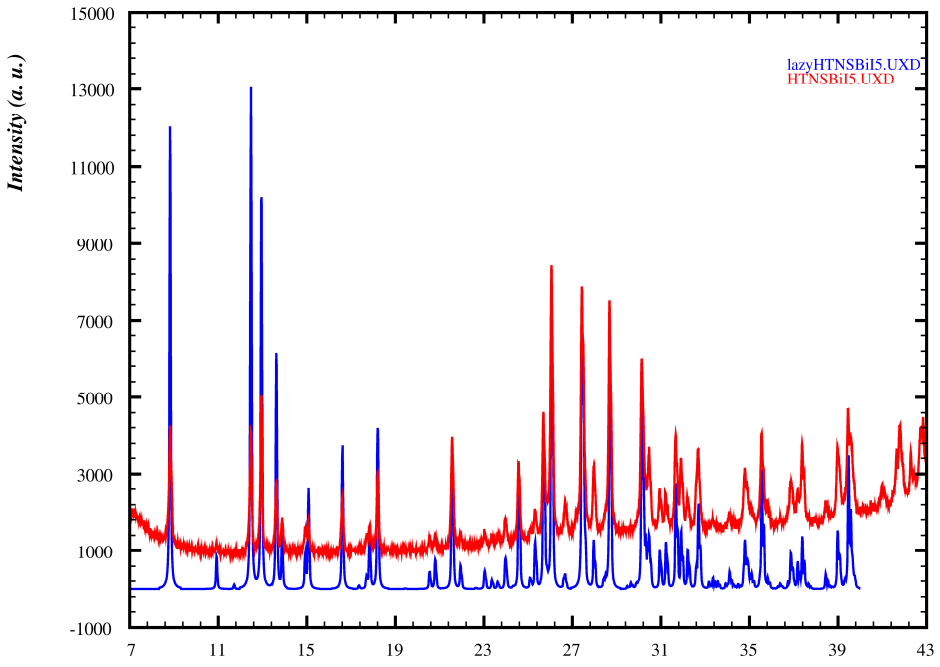
Table 3. Anisotropic displacement parameters (A^2 x 10^3) for 1b
The anisotropic displacement factor exponent takes the form:
-2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
Bi	37(1)	35(1)	47(1)	-7(1)	-3(1)	2(1)
I(2)	51(1)	70(1)	86(1)	-8(1)	8(1)	23(1)
I(3)	87(1)	69(1)	65(1)	24(1)	-2(1)	0(1)
I(5)	61(1)	58(1)	50(1)	10(1)	-2(1)	8(1)
I(4)	59(1)	84(1)	66(1)	-19(1)	5(1)	32(1)
I(1)	67(1)	62(1)	110(1)	-22(1)	-30(1)	-14(1)
S	89(2)	99(3)	132(3)	42(2)	36(2)	12(2)
C(1)	69(8)	134(11)	82(8)	-9(8)	5(8)	6(8)
N	76(6)	131(9)	89(7)	45(7)	-6(5)	-12(6)
C(4)	156(13)	51(7)	159(12)	-4(7)	11(12)	7(8)
C(3)	250(20)	143(14)	147(13)	-30(11)	-14(17)	-87(17)
C(2)	59(8)	224(18)	175(14)	98(14)	47(9)	31(9)

Table 4 - Hydrogen bonds with H..A < r(A) + 2.000 Angstroms and <DHA > 110 deg.

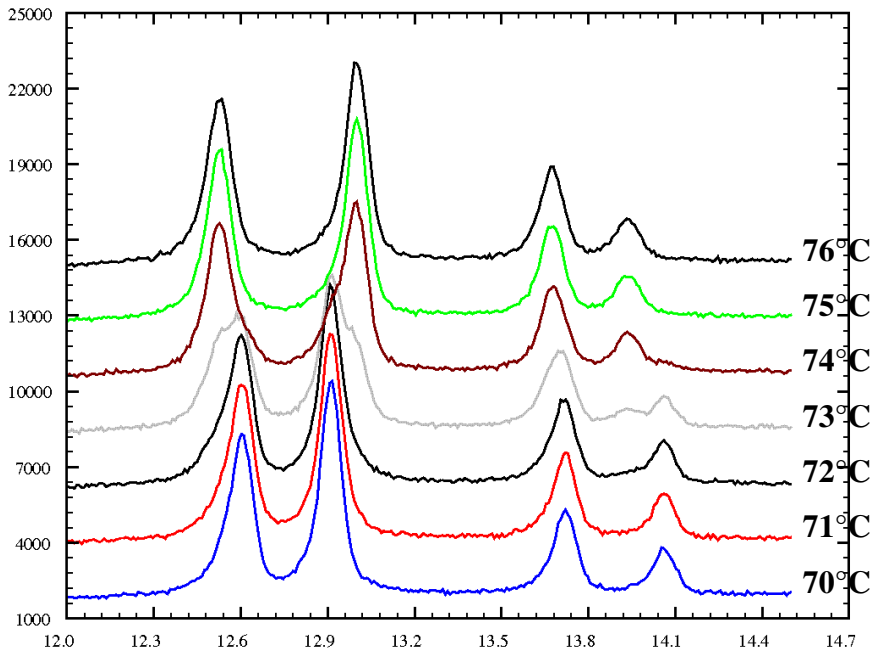
D-H	d(D-H)	d(H..A)	<DHA	d(D..A)	A
N-H0A	0.890	2.972	136.53	3.669	I4 [-x+1, y-1/2, -z+1/2]
N-H0A	0.890	3.036	131.21	3.684	I3 [-x+3/2, -y+2, z-1/2]
N-H0B	0.890	3.206	119.14	3.722	I4 [-x+3/2, -y+2, z-1/2]
N-H0B	0.890	3.295	150.50	4.094	I2 [-x+2, y-1/2, -z+1/2]
N-H0C	0.890	3.130	113.39	3.578	I5 [-x+2, y-1/2, -z+1/2]
N-H0C	0.890	3.248	153.20	4.062	I2

IV-D- XRPD: theoretical (blue) and experimental (red)

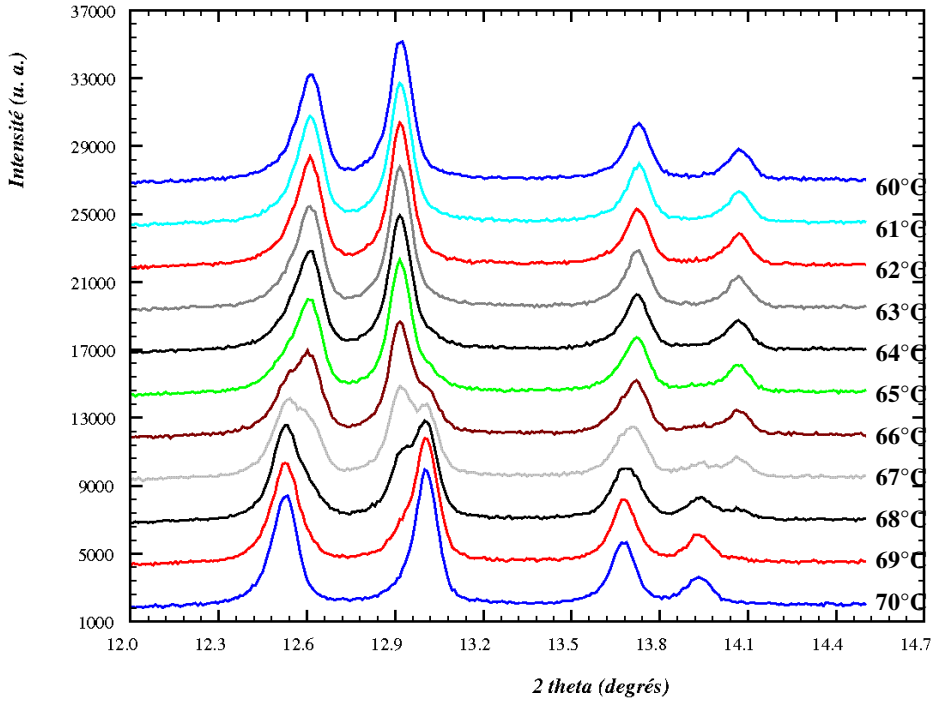


IV-E- XRPD= f(T)

1- Increasing of temperature, from 70°C to 76°C (12-15°2θ range)



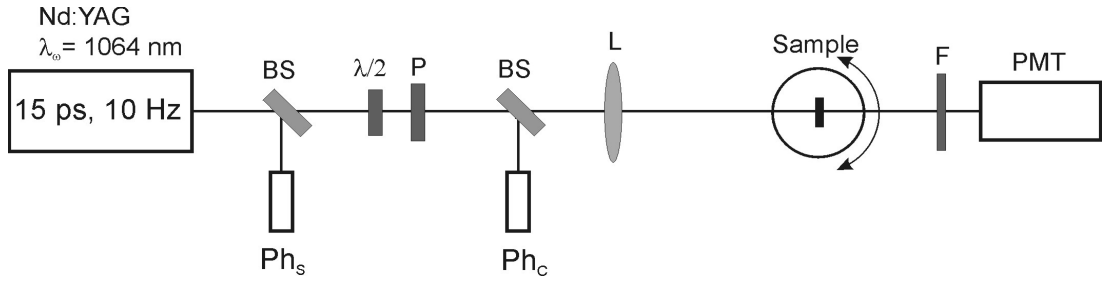
2- Decreasing of temperature, from 70°C to 60°C (12-15°2θ range)



V – ONL properties

The properties of the Second Harmonic Generation (SHG) were studied for a fundamental wavelength at 1064 nm generated by a Q-switch Nd:YAG laser (Model Continuum Leopard D-10) with a pulse duration of 16 ps and a average density power of 0.2 mJ per pulse at the repetition frequency of 10 Hz using Kurtz and Perry test, on sample of **1a** and **2**. The power of the fundamental beam was changed with a half-wave plate and a Glan polarizer. The beam was focused on the sample by a convergent lens with a focal length of 250 mm. The sample was rotated by using a stepped motor monitored by a power station of acquisition with an angle resolution up to 0.04°. The SH signal was detected by a photomultiplier tube (Hamamatsu R1828-01), then integrated by a boxcar integrate and processed by a computer. A *y-cut* quartz substrate was used as reference sample to calibrate the experimental setup.

The experimental setup for the SHG is described on the following figure:



BS: dichroic beam splitters
λ/2: half-wave plate
P: Glan polarizer
L: convergent lens
F: selective filter at 532 nm
PMT: tube photomultiplier
Phs: synchronization photodiode
Phc: control photodiode

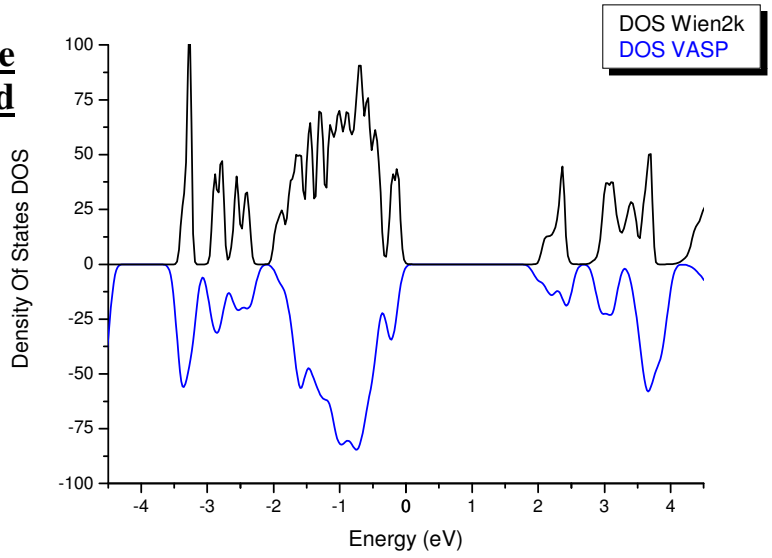
VI- Calculations

VI-A Structural optimizations

It was necessary to optimize the geometries in order to check whether the DFT level of theory was accurate enough or not to reproduce the structures, this step being necessary before arguing about the electronic structures of compounds **1** and **3**. Hybrid compounds possess organic and inorganic parts, so there will be three points to distinguish between the initial and optimized geometries: differences within the organic cations, differences concerning the Bi-I distances and finally the non-bonding hydrogen interactions at the interface of the organic and inorganic moieties.

Structural optimizations of the organic molecules were successful. The main average bond lengths are: $d_{C\text{-}C}$=1.52 Å, $d_{C\text{-}N}$=1.49 Å, $d_{C\text{-}S}$=1.80 Å, $d_{C\text{-}H}$=1.10 Å and $d_{N\text{-}H}$=1.05 Å. For the C-C, C-N and C-S distances, the deviation compared to the experimental values is less than 2% whereas for the C-H and N-H distances, the optimized bond lengths are more than 10% longer than the crystallographic ones. This discrepancy for hydrogen atoms is totally normal as the accuracy on their position obtained from the X-ray diffraction is very low. Indeed, the C-H (or N-H) bond lengths are usually underestimated by X-ray diffraction according to their mean square atomic displacement which makes these atoms appear artificially nearer than they are. Looking at the Bi-I distances, the results of the DFT optimization are also satisfying since the average difference is less than 1% (equatorial distances $d_{Bi\text{-}I1}$=2.98 Å, $d_{Bi\text{-}I2}$=3.00 Å, $d_{Bi\text{-}I4}$=3.21 Å, $d_{Bi\text{-}I4\#1}$=3.24 Å, axial distances $d_{Bi\text{-}I3}$=3.10 Å, $d_{Bi\text{-}I5}$=3.09 Å for compound **1a**). The last point to discuss is the interactions between the organic and inorganic parts. Those hybrid salts are based on strong electrostatic interactions highlighted by hydrogen bonds at the interface. The optimized hydrogen bonds after the structural relaxations are, in average, shorter by less than 4% than the initial ones. A special feature of the **1a** compound is the short I...I contact between BiI_5 ribbons so it was important to check the interchains I…I distances are correctly modelled. The optimized distances are $d_{I1\text{-}I3}$=3.90 Å and $d_{I3\text{-}I5}$=3.94 Å and according to the crystallographic ones ($d_{I1\text{-}I3}$=3.94 Å, $d_{I3\text{-}I5}$=3.97 Å, Figure 1) the understimation is less than 1% which is very satisfying. In average, the deviation compared to the experimental value is less than 3% for the bond distances for each part and this crystallographic features analysis allows us to conclude that the DFT calculations are accurate enough to describe the structures of these hybrid compounds and also that reliable parameters could be extracted from the electronic and band structures analysis.

VI-B Comparison of the total DOS of 1a calculated using VASP and Wien2k



VI-C Model compounds: input files and band structures

VI-C1-CIF File of 1a

```
data_1a
_cell_length_a   8.4750
_cell_length_b  12.6140
_cell_length_c  16.3850
_cell_angle_alpha   90.000
_cell_angle_beta   90.000
_cell_angle_gamma   90.000
_symmetry_space_group_name_H-M 'P21cn'
loop_
_atom_site_label
_atom_site_type_symbol
_atom_site_fract_x
_atom_site_fract_y
_atom_site_fract_z
Bi  Bi    0.7957596   0.3419483   0.4237520
I   I     0.5683988   0.1858073   0.3536374
I   I     0.0894471   0.2264894   0.3723455
I   I     0.8159567   0.4812964   0.2681314
I   I     0.4928297   0.4735101   0.4842543
I   I     0.7821327   0.2264420   0.5896341
Na   Na    0.7228588   0.4820525   0.6825179
Na   Na    0.7324356   0.6150181   0.8664275
```

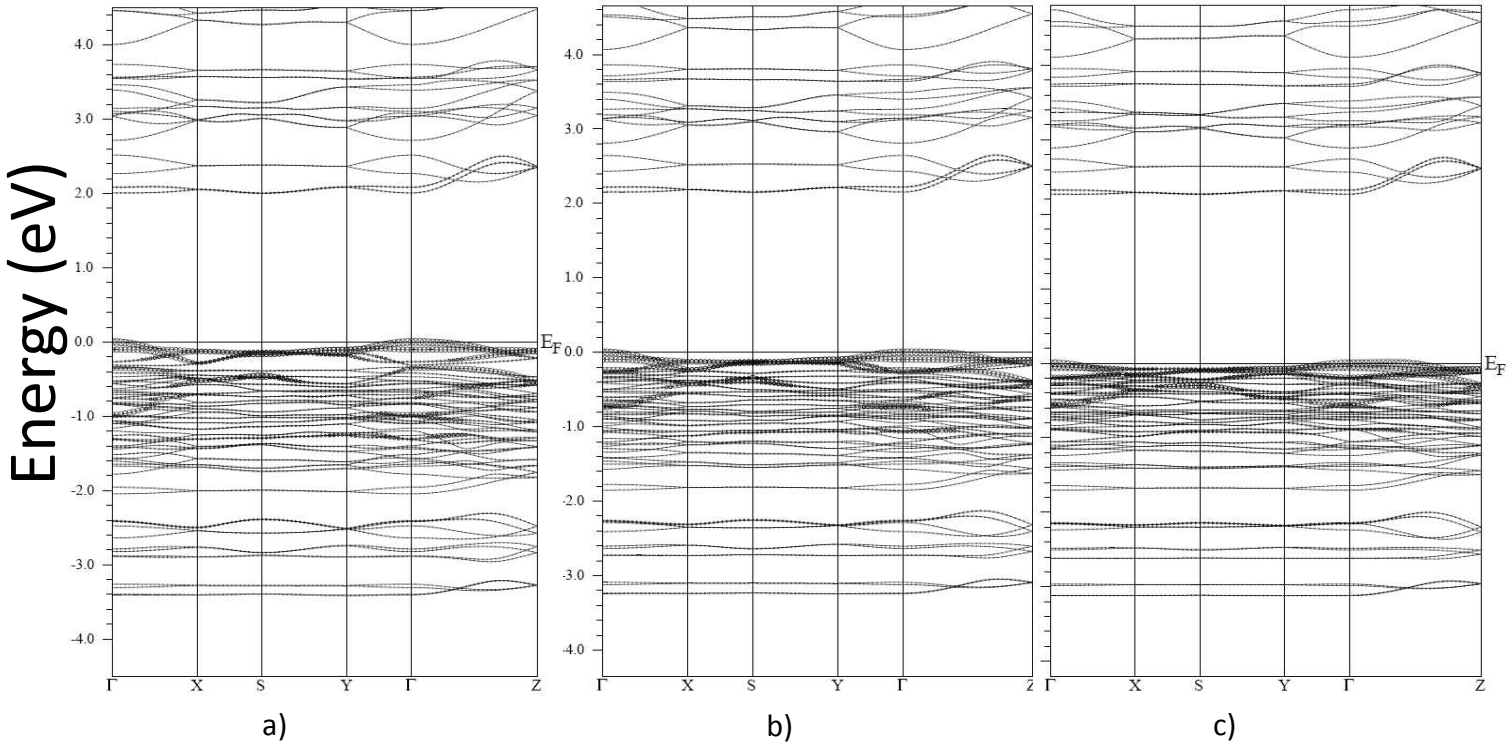
VI-C2-CIF File of 1a+2.5%

```
data_1a+2.5%
_cell_length_a 8.4750
_cell_length_b          12.9293
_cell_length_c16.7946
_cell_angle_alpha      90.000
_cell_angle_beta       90.000
_cell_angle_gamma   90.000
_symmetry_space_group_name_H-M          'P 21 c n'
loop_
_atom_site_label
_atom_site_type_symbol
_atom_site_fract_x
_atom_site_fract_y
_atom_site_fract_z
Bi1 Bi  0.7958  0.1542 -0.0744
I1  I   0.5684  0.3065 -0.1428
I2  I   1.0895  0.2668 -0.1245
I3  I   0.8160  0.0182 -0.2262
I4  I   0.9928 -0.0258  0.0154
I5  I   0.7821  0.2669  0.0874
Na1 Na  0.7229  0.0175  0.1781
Na2 Na  0.2324  0.3756  0.1303
```

VI-C3-CIF File of 1a+5%

```
data_1a+5%
_cell_length_a 8.4750
_cell_length_b          13.2447
_cell_length_c17.2042
_cell_angle_alpha       90.000
_cell_angle_beta        90.000
_cell_angle_gamma       90.000
_symmetry_space_group_name_H-M          'P 21 c n'
loop_
_atom_site_label
_atom_site_type_symbol
_atom_site_fract_x
_atom_site_fract_y
_atom_site_fract_z
Bi1 Bi  0.7958  0.1505 -0.0726
I1  I   0.5684  0.2992 -0.1394
I2  I   1.0895  0.2605 -0.1216
I3  I   0.8160  0.0178 -0.2208
I4  I   0.9928 -0.0252  0.0150
I5  I   0.7821  0.2605  0.0854
Na1 Na  0.7229  0.0171  0.1738
Na2 Na  0.2324  0.3666  0.1272
```

VI – B4 - Figure. Band structures of **1** (a) and of relative model compounds 1a2.5 (b) and 1a5.0 (c). The bottom of the VB is chosen as energy reference.



VI-D compound 3: $(HO_2C(C_6H_4)CH_2NH_3)BiI_4$

Figure Isosurface of the charge density corresponding to the highest occupied states for compound **3** showing the anti bonding interactions between the iodine 5p states and the bismuth 6s orbitals.