# The effect of ring substituent position on the structural and optoelectronic properties of novel quasi low-dimensional hybrid 2-, 3-, and 4-(bromomethyl)pyridinium lead bromides

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## Supplementary material

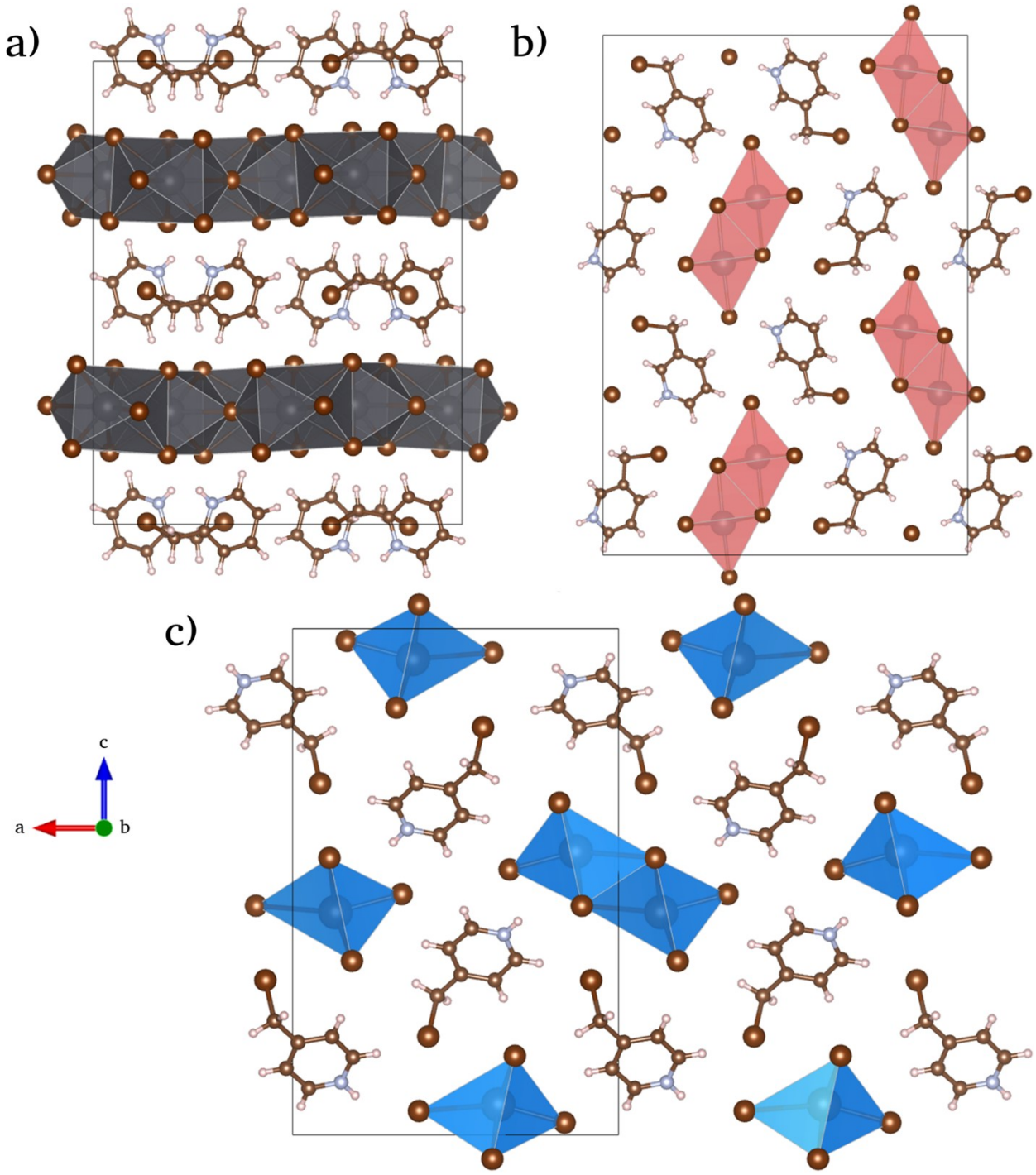
a)
b)
c)
c
a
b

Figure S1. Organic cation orientations in 2- (a), 3- (b), and 4-(Bromomethyl)pyridinim (c) lead bromides.

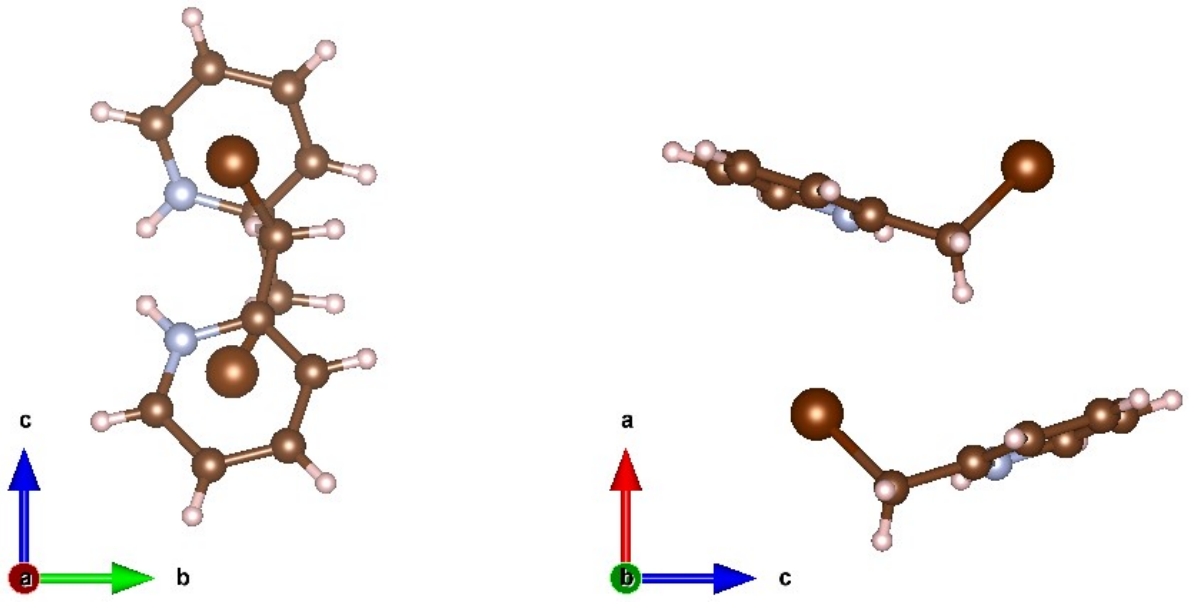

Figure S2. Mutual orientation of organic cations in 2-(Bromomethyl)pyridinim lead bromide.

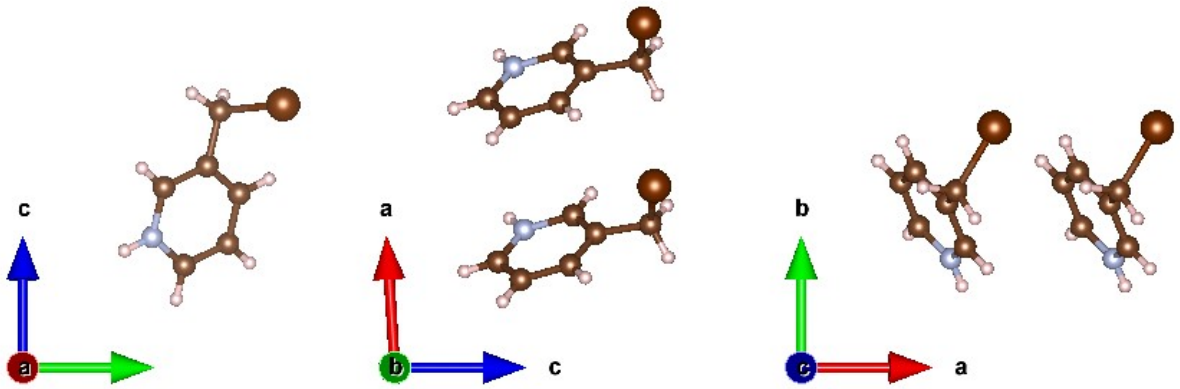


Figure S3. Mutual orientation of organic cations in 3-(Bromomethyl)pyridinim lead bromide.

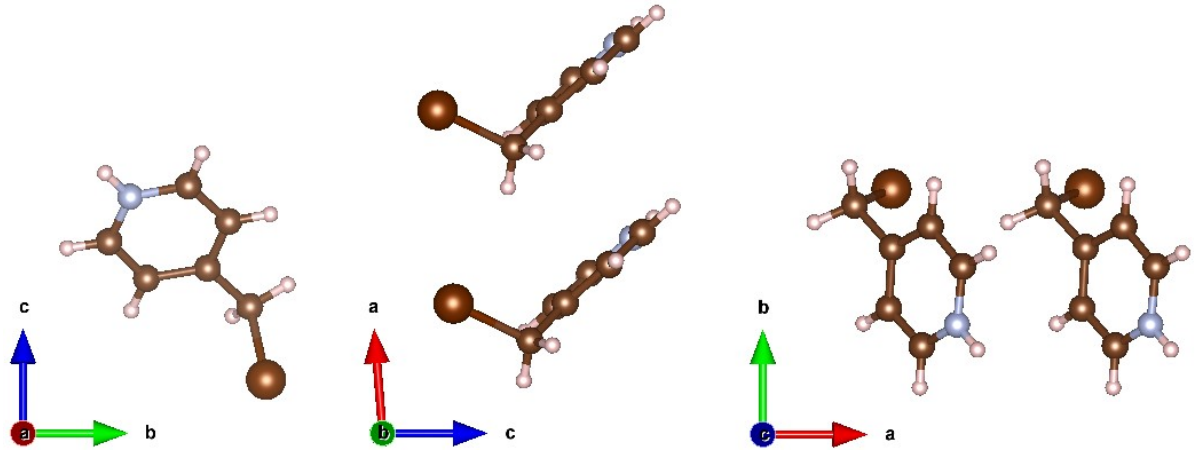


Figure S4. Mutual orientation of organic cations in 4-(Bromomethyl)pyridinim lead bromide.

Table S1. Crystal data and structure refinement for $(2\text{-}BrCH_2PyH)Pb_2Br_5$ at 173 K.

| | |
|---|---|
| Empirical formula | C6 H7 Br6 N Pb2 |
| Formula weight | 986.9 |
| Temperature | 173 K |
| Wavelength | 0.71073 Å |
| Crystal system | orthorhombic |
| Space group | P b c a |
| Unit cell dimensions | a = 17.1340(5) Å, α = 90°<br>b = 8.4626(3) Å, β = 90°<br>c = 21.4906(6) Å, γ = 90° |

| | |
|---|---|
| Volume | 3116.10(17) $Å^3$ |
| Z | 8 |
| Density (calculated) | 4.2074 $g/cm^3$ |
| Absorption coefficient | 36.942 $mm^{-1}$ |
| F(000) | 3392 |
| Crystal size | 0.102 x 0.101 x 0.085 $mm^3$ |
| θ range for data collection | 1.9 to 33.73° |
| Index ranges | -25<=h<=26, -13<=k<=12, -28<=l<=31 |
| Reflections collected | 41900 |
| Independent reflections | 2806 [$R_{int}$ = 0.2267] |
| Completeness to θ = 31.54° | 98% |
| Refinement method | F |
| Data / restraints / parameters | 2806 / 0 / 137 |
| Goodness-of-fit | 2.36 |
| Final R indices [I>2σ(I)] | $R_{obs}$ = 0.0611, $wR_{obs}$ = 0.0804 |
| R indices [all data] | $R_{all}$ = 0.0684, $wR_{all}$ = 0.0809 |
| Extinction coefficient | 7200(300) |
| Largest diff. peak and hole | 4.21 and -4.63 $e \cdot Å^{-3}$ |

$R = \Sigma||F_o|-|F_c|| / \Sigma|F_o|$, $wR = \{\Sigma[w(|F_o|^2 - |F_c|^2)^2] / \Sigma[w(|F_o|^4)]\}^{1/2}$ and $w=1/(\sigma^2(F)+0.0001F^2)$

Table S2. Atomic coordinates ($x10^4$) and equivalent isotropic displacement parameters ($Å^2x10^3$) for (2-$BrCH_2PyH)Pb_2Br_5$ at 173 K with estimated standard deviations in parentheses.

| Label | x | y | z | Occupancy | $U_{eq}$* |
|---|---|---|---|---|---|
| Pb(1) | 2072(1) | 6012(2) | 2577(1) | 1 | 27(1) |
| Pb(2) | 4629(1) | 4424(2) | 2465(1) | 1 | 27(1) |
| Br(1) | 3547(2) | 3121(3) | -45(1) | 1 | 37(1) |
| Br(2) | 1244(1) | 2707(3) | 2564(1) | 1 | 26(1) |
| Br(3) | 578(2) | 6192(3) | 1639(1) | 1 | 25(1) |
| Br(4) | 2989(2) | 4294(3) | 3494(1) | 1 | 27(1) |
| Br(5) | 2963(2) | 4302(3) | 1680(1) | 1 | 25(1) |
| Br(6) | 5447(2) | 6125(3) | 1555(1) | 1 | 29(1) |
| C(1) | 2799(12) | 1660(30) | 307(10) | 1 | 37(8) |
| C(2) | 1984(12) | 2140(20) | 156(8) | 1 | 23(6) |
| C(3) | 1450(12) | 2630(30) | 600(9) | 1 | 28(7) |
| N(1) | 1770(10) | 2150(20) | -447(7) | 1 | 29(6) |
| C(4) | 1076(11) | 2570(30) | -652(10) | 1 | 29(7) |
| C(5) | 526(12) | 3060(30) | -224(9) | 1 | 42(9) |
| C(6) | 715(12) | 3090(30) | 398(9) | 1 | 30(7) |
| H(1) | 2896.06 | 619.21 | 148.21 | 1 | 44.9 |
| H(2) | 2863.72 | 1624.14 | 750.21 | 1 | 44.9 |
| H(3) | 1585.27 | 2656.59 | 1033.13 | 1 | 33.5 |
| H(4) | 2114.51 | 1858.75 | -720.83 | 1 | 34.2 |
| H(5) | 956.82 | 2547.29 | -1088.41 | 1 | 34.9 |
| H(6) | 13.63 | 3365.03 | -358.31 | 1 | 50.7 |
| H(7) | 334.67 | 3436.84 | 695.58 | 1 | 36.2 |

*$U_{eq}$ is defined as one third of the trace of the orthogonalized $U_{ij}$ tensor.

Table S3. Anisotropic displacement parameters ($Å^2x10^3$) for (2-$BrCH_2PyH)Pb_2Br_5$ at 173 K with estimated standard deviations in parentheses.

| Labe | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{12}$ | $U_{13}$ | $U_{23}$ |
|---|---|---|---|---|---|---|
| Pb(1) | 27(1) | 27(1) | 28(1) | 5(1) | 0(1) | 0(1) |
| Pb(2) | 26(1) | 26(1) | 29(1) | -3(1) | 1(1) | 1(1) |
| Br(1) | 26(2) | 41(2) | 45(2) | -1(2) | 1(1) | 3(2) |
| Br(2) | 20(1) | 19(2) | 39(2) | 0(1) | 1(1) | 0(1) |
| Br(3) | 24(1) | 27(2) | 24(1) | -1(1) | 0(1) | 2(1) |
| Br(4) | 26(1) | 30(2) | 24(1) | -1(1) | -1(1) | 5(1) |
| Br(5) | 24(1) | 28(2) | 24(1) | 2(1) | 1(1) | -2(1) |
| Br(6) | 27(1) | 33(2) | 26(1) | -2(1) | 2(1) | 6(1) |
| C(1) | 37(12) | 28(15) | 47(13) | 2(11) | -5(11) | 19(11) |
| C(2) | 32(11) | 13(11) | 24(10) | 0(9) | 3(8) | -3(8) |
| C(3) | 34(11) | 20(13) | 29(11) | -2(10) | 0(9) | -1(9) |
| N(1) | 32(10) | 25(11) | 29(9) | -10(8) | 5(7) | -2(8) |
| C(4) | 31(11) | 22(13) | 34(11) | -8(9) | -6(9) | 4(9) |
| C(5) | 25(11) | 70(20) | 29(11) | -4(12) | 1(9) | 5(12) |
| C(6) | 25(11) | 26(14) | 40(12) | 0(10) | 9(9) | -4(10) |

The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11} + ... + 2hka^*b^*U_{12}]$.

Table S4. Bond lengths [Å] for (2-$BrCH_2PyH)Pb_2Br_5$ at 173 K with estimated standard deviations in parentheses.

| Label | Distances |
|---|---|
| Pb(1)-Br(2) | 3.136(2) |
| Pb(1)-Br(2)#1 | 3.223(2) |
| Pb(1)-Br(3) | 3.261(2) |
| Pb(1)-Br(4) | 2.910(2) |
| Pb(1)-Br(5) | 2.853(2) |
| Pb(1)-Br(5)#1 | 3.387(2) |
| Pb(1)-Br(6)#2 | 3.353(2) |
| Pb(2)-Br(2)#3 | 3.126(2) |
| Pb(2)-Br(2)#1 | 3.162(2) |
| Pb(2)-Br(3)#3 | 2.931(2) |
| Pb(2)-Br(3)#4 | 3.280(2) |
| Pb(2)-Br(5) | 3.318(2) |
| Pb(2)-Br(6) | 2.802(2) |
| Br(1)-C(1) | 1.93(2) |
| Br(1)-N(1) | 3.270(17) |
| Br(1)-N(1)#1 | 3.560(19) |
| Br(4)-N(1)#5 | 3.795(18) |
| Br(4)-N(1)#6 | 3.323(17) |
| C(1)-C(2) | 1.49(3) |
| C(1)-H(1) | 0.96 |
| C(1)-H(2) | 0.96 |
| C(2)-C(3) | 1.39(3) |
| C(2)-N(1) | 1.35(2) |
| C(3)-C(6) | 1.39(3) |
| C(3)-H(3) | 0.96 |
| N(1)-C(4) | 1.32(3) |
| N(1)-H(4) | 0.87 |
| C(4)-C(5) | 1.38(3) |
| C(4)-H(5) | 0.96 |
| C(5)-C(6) | 1.37(3) |
| C(5)-H(6) | 0.96 |
| C(6)-H(7) | 0.96 |

Symmetry transformations used to generate equivalent atoms:

(1) -x+1/2,y+1/2,z (2) x-1/2,y,-z+1/2 (3) x+1/2,y,-z+1/2 (4) -x+1/2,y-1/2,z (5) -x+1/2,-y+1,z+1/2 (6) x,-y+1/2,z+1/2 (7) -x+1/2,-y+1,z-1/2 (8) x,-y+1/2,z-1/2

Table S5. Bond angles [°] for (2-$BrCH_2PyH)Pb_2Br_5$ at 173 K with estimated standard deviations in parentheses.

| Label | Angles | Label | Angles |
|---|---|---|---|
| Br(2)-Pb(1)-Br(2)#1 | 143.31(6) | C(1)-Br(1)-N(1) | 47.6(7) |
| Br(2)-Pb(1)-Br(3) | 71.41(6) | C(1)-Br(1)-N(1)#1 | 127.3(7) |
| Br(2)-Pb(1)-Br(4) | 78.74(6) | N(1)-Br(1)-N(1)#1 | 92.0(4) |
| Br(2)-Pb(1)-Br(5) | 77.50(6) | Pb(1)-Br(2)-Pb(1)#4 | 89.54(5) |
| Br(2)-Pb(1)-Br(5)#1 | 136.07(5) | Pb(1)-Br(2)-Pb(2)#2 | 89.19(6) |
| Br(2)-Pb(1)-Br(6)#2 | 69.81(6) | Pb(1)-Br(2)-Pb(2)#4 | 176.38(7) |
| Br(2)#1-Pb(1)-Br(3) | 132.57(6) | Pb(1)#4-Br(2)-Pb(2)#2 | 178.59(8) |
| Br(2)#1-Pb(1)-Br(4) | 75.22(6) | Pb(1)#4-Br(2)-Pb(2)#4 | 91.89(6) |
| Br(2)#1-Pb(1)-Br(5) | 74.98(6) | Pb(2)#2-Br(2)-Pb(2)#4 | 89.34(5) |
| Br(2)#1-Pb(1)-Br(5)#1 | 69.18(5) | Pb(1)-Br(3)-Pb(2)#2 | 90.30(5) |
| Br(2)#1-Pb(1)-Br(6)#2 | 137.37(6) | Pb(1)-Br(3)-Pb(2)#1 | 77.84(5) |
| Br(3)-Pb(1)-Br(4) | 149.97(7) | Pb(2)#2-Br(3)-Pb(2)#1 | 90.57(5) |
| Br(3)-Pb(1)-Br(5) | 91.48(5) | Pb(1)-Br(4)-N(1)#5 | 94.0(3) |
| Br(3)-Pb(1)-Br(5)#1 | 66.19(5) | Pb(1)-Br(4)-N(1)#6 | 108.0(3) |
| Br(3)-Pb(1)-Br(6)#2 | 71.99(5) | N(1)#5-Br(4)-N(1)#6 | 87.1(4) |
| Br(4)-Pb(1)-Br(5) | 85.16(6) | Pb(1)-Br(5)-Pb(1)#4 | 91.31(6) |
| Br(4)-Pb(1)-Br(5)#1 | 143.67(6) | Pb(1)-Br(5)-Pb(2) | 95.79(6) |
| Br(4)-Pb(1)-Br(6)#2 | 94.92(6) | Pb(1)#4-Br(5)-Pb(2) | 75.59(5) |
| Br(5)-Pb(1)-Br(5)#1 | 92.38(6) | Pb(1)#3-Br(6)-Pb(2) | 90.72(6) |
| Br(5)-Pb(1)-Br(6)#2 | 146.59(7) | Br(1)-C(1)-C(2) | 111.3(16) |
| Br(5)#1-Pb(1)-Br(6)#2 | 106.19(6) | Br(1)-C(1)-H(1) | 109.47 |
| Br(2)#3-Pb(2)-Br(2)#1 | 145.93(6) | Br(1)-C(1)-H(2) | 109.47 |
| Br(2)#3-Pb(2)-Br(3)#3 | 76.05(6) | C(2)-C(1)-H(1) | 109.47 |
| Br(2)#3-Pb(2)-Br(3)#4 | 72.39(5) | C(2)-C(1)-H(2) | 109.47 |
| Br(2)#3-Pb(2)-Br(5) | 137.50(6) | H(1)-C(1)-H(2) | 107.58 |
| Br(2)#3-Pb(2)-Br(6) | 77.44(6) | C(1)-C(2)-C(3) | 123.4(17) |
| Br(2)#1-Pb(2)-Br(3)#3 | 76.70(6) | C(1)-C(2)-N(1) | 117.9(17) |
| Br(2)#1-Pb(2)-Br(3)#4 | 135.88(5) | C(3)-C(2)-N(1) | 118.7(18) |
| Br(2)#1-Pb(2)-Br(5) | 69.79(5) | C(2)-C(3)-C(6) | 117.9(18) |
| Br(2)#1-Pb(2)-Br(6) | 80.35(6) | C(2)-C(3)-H(3) | 121.07 |
| Br(3)#3-Pb(2)-Br(3)#4 | 147.25(6) | C(6)-C(3)-H(3) | 121.07 |
| Br(3)#3-Pb(2)-Br(5) | 145.84(6) | Br(1)-N(1)-Br(1)#4 | 108.6(5) |
| Br(3)#3-Pb(2)-Br(6) | 85.36(6) | Br(1)-N(1)-Br(4)#7 | 81.8(4) |
| Br(3)#4-Pb(2)-Br(5) | 66.79(5) | Br(1)-N(1)-Br(4)#8 | 71.8(3) |
| Br(3)#4-Pb(2)-Br(6) | 96.03(6) | Br(1)-N(1)-C(2) | 59.6(10) |
| Br(5)-Pb(2)-Br(6) | 95.26(6) | Br(1)-N(1)-C(4) | 149.4(14) |

| Label | Angles | Label | Angles |
|---|---|---|---|
| Br(1)#4-N(1)-Br(4)#8 | 84.8(4) | C(2)-N(1)-H(4) | 117.61 |
| Br(1)#4-N(1)-C(2) | 78.5(12) | C(4)-N(1)-H(4) | 117.61 |
| Br(1)#4-N(1)-C(4) | 101.8(13) | N(1)-C(4)-C(5) | 118.3(19) |
| Br(1)#4-N(1)-H(4) | 89.72 | N(1)-C(4)-H(5) | 120.86 |
| Br(4)#7-N(1)-Br(4)#8 | 79.2(3) | C(5)-C(4)-H(5) | 120.87 |
| Br(4)#7-N(1)-C(2) | 123.6(13) | C(4)-C(5)-C(6) | 120(2) |
| Br(4)#7-N(1)-C(4) | 71.5(12) | C(4)-C(5)-H(6) | 120.24 |
| Br(4)#7-N(1)-H(4) | 75.25 | C(6)-C(5)-H(6) | 120.24 |
| Br(4)#8-N(1)-C(2) | 119.0(12) | C(3)-C(6)-C(5) | 120.9(19) |
| Br(4)#8-N(1)-C(4) | 116.0(12) | C(3)-C(6)-H(7) | 119.57 |
| Br(4)#8-N(1)-H(4) | 5.63 | C(5)-C(6)-H(7) | 119.57 |
| C(2)-N(1)-C(4) | 124.8(18) | | |

Symmetry transformations used to generate equivalent atoms:

(1) -x+1/2,y+1/2,z (2) x-1/2,y,-z+1/2 (3) x+1/2,y,-z+1/2 (4) -x+1/2,y-1/2,z (5) -x+1/2,-y+1,z+1/2 (6) x,-y+1/2,z+1/2 (7) -x+1/2,-y+1,z-1/2 (8) x,-y+1/2,z-1/2

Table S6. Crystal data and structure refinement for (3-$BrCH_2PyH)PbBr_3$ at 173(2) K.

| | |
|---|---|
| Empirical formula | C6 H7 Br4 N Pb |
| Formula weight | 619.96 |
| Temperature | 173(2) K |
| Wavelength | 0.71073 Å |
| Crystal system | monoclinic |
| Space group | $P2_1/c$ |
| Unit cell dimensions | a = 4.3364(3) Å, α = 90°<br>b = 19.7860(15) Å, β = 93.675(2)°<br>c = 14.1395(11) Å, γ = 90° |
| Volume | 1210.67(16) $Å^3$ |
| Z | 4 |
| Density (calculated) | 3.401 $g/cm^3$ |
| Absorption coefficient | 27.090 $mm^{-1}$ |
| F(000) | 1088 |
| Crystal size | 0.085 x 0.065 x 0.054 $mm^3$ |
| θ range for data collection | 1.773 to 26.000° |
| Index ranges | -4<=h<=5, -24<=k<=24, -17<=l<=17 |
| Reflections collected | 11966 |
| Independent reflections | 2379 [$R_{int}$ = 0.0453] |
| Completeness to θ = 25.242° | 99.5% |
| Refinement method | Full-matrix least-squares on $F^2$ |
| Data / restraints / parameters | 2379 / 0 / 109 |
| Goodness-of-fit | 1.173 |
| Final R indices [I > 2σ(I)] | $R_{obs}$ = 0.0467, $wR_{obs}$ = 0.1376 |
| R indices [all data] | $R_{all}$ = 0.0540, $wR_{all}$ = 0.1505 |
| Extinction coefficient | . |
| Largest diff. peak and hole | 3.440 and -2.224 e·$Å^{-3}$ |

$R = \Sigma||F_o|-|F_c|| / \Sigma|F_o|$, $wR = \{\Sigma[w(|F_o|^2 - |F_c|^2)^2] / \Sigma[w(|F_o|^4)]\}^{1/2}$ and $w=1/[\sigma^2(Fo^2)+(0.0791P)^2+29.5929P]$ where $P=(Fo^2+2Fc^2)/3$

Table S7. Atomic coordinates ($x10^4$) and equivalent isotropic displacement parameters ($Å^2x10^3$) for (3-$BrCH_2PyH$)$PbBr_3$ at 173(2) K with estimated standard deviations in parentheses.

| Label | x | y | z | Occupancy | $U_{eq}$* |
|---|---|---|---|---|---|
| Pb(1) | 7847(2) | 4529(1) | 1273(1) | 1 | 18(1) |
| Br(1) | 12584(3) | 5613(1) | 945(1) | 1 | 22(1) |
| Br(2) | 12705(3) | 3509(1) | 1320(1) | 1 | 22(1) |
| Br(3) | 8832(3) | 4697(1) | 3343(1) | 1 | 25(1) |
| Br(4) | 7413(4) | 7761(1) | 6385(1) | 1 | 34(1) |
| N(1) | 4780(30) | 5984(6) | 3941(10) | 1 | 29(3) |
| H1N() | 5410.29 | 5595.8 | 3719.42 | 1 | 35 |
| C(1) | 2030(30) | 6995(8) | 3693(10) | 1 | 27(3) |
| H1C() | 806.23 | 7288.9 | 3292.89 | 1 | 32 |
| C(2) | 2790(30) | 7171(7) | 4625(10) | 1 | 23(3) |
| H(2) | 2107.25 | 7592.62 | 4858.36 | 1 | 28 |
| C(3) | 5330(40) | 6891(7) | 6246(10) | 1 | 26(3) |
| H(3A) | 6688.24 | 6531.09 | 6521.96 | 1 | 31 |
| H(3AB) | 3417.72 | 6898.67 | 6593.83 | 1 | 31 |
| C(4) | 3050(40) | 6393(8) | 3351(11) | 1 | 31(3) |
| H(4) | 2560.37 | 6265.53 | 2711.36 | 1 | 37 |
| C(5) | 4530(30) | 6742(7) | 5227(10) | 1 | 21(3) |
| C(6) | 5590(30) | 6141(7) | 4851(11) | 1 | 25(3) |
| H(6) | 6868.65 | 5844.88 | 5232.3 | 1 | 30 |

*$U_{eq}$ is defined as one third of the trace of the orthogonalized $U_{ij}$ tensor.

Table S8. Anisotropic displacement parameters ($Å^2x10^3$) for (3-$BrCH_2PyH$)$PbBr_3$ at 173(2) K with estimated standard deviations in parentheses.

| Label | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{12}$ | $U_{13}$ | $U_{23}$ |
|---|---|---|---|---|---|---|
| Pb(1) | 18(1) | 20(1) | 18(1) | -1(1) | 1(1) | 1(1) |
| Br(1) | 26(1) | 19(1) | 20(1) | -3(1) | 1(1) | -2(1) |
| Br(2) | 23(1) | 18(1) | 25(1) | 0(1) | 0(1) | -1(1) |
| Br(3) | 30(1) | 23(1) | 20(1) | 6(1) | -1(1) | -1(1) |
| Br(4) | 47(1) | 30(1) | 23(1) | -1(1) | -6(1) | -6(1) |
| N(1) | 28(7) | 17(6) | 43(8) | 3(5) | 3(6) | -7(5) |
| C(1) | 38(8) | 26(8) | 18(7) | 4(6) | 6(6) | -4(5) |
| C(2) | 32(7) | 16(6) | 21(7) | 4(6) | 4(6) | -2(5) |
| C(3) | 32(8) | 26(7) | 19(7) | -2(6) | -3(6) | -1(6) |
| C(4) | 39(9) | 31(8) | 22(8) | 11(7) | 1(7) | -2(6) |
| C(5) | 25(7) | 16(6) | 22(7) | 8(5) | 4(6) | 2(5) |
| C(6) | 26(7) | 19(7) | 32(8) | 4(6) | 5(6) | -2(6) |

The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11} + ... + 2hka^*b^*U_{12}]$.

Table S9. Bond lengths [Å] for (3-$BrCH_2PyH$)$PbBr_3$ at 173(2) K with estimated standard deviations in parentheses.

| Label | Distances | Label | Distances |
|---|---|---|---|
| Pb(1)-Br(2) | 2.9155(14) | C(1)-C(2) | 1.382(19) |
| Pb(1)-Br(3) | 2.9486(15) | C(1)-H1C() | 0.9500 |
| Pb(1)-Br(2)#1 | 3.0122(14) | C(2)-C(5) | 1.391(19) |
| Pb(1)-Br(1) | 3.0252(14) | C(2)-H(2) | 0.9500 |
| Pb(1)-Br(1)#2 | 3.1428(14) | C(3)-C(5) | 1.489(19) |
| Pb(1)-Br(1)#1 | 3.1436(15) | C(3)-H(3A) | 0.9900 |
| Br(4)-C(3) | 1.948(14) | C(3)-H(3AB) | 0.9900 |
| N(1)-C(6) | 1.35(2) | C(4)-H(4) | 0.9500 |
| N(1)-C(4) | 1.354(19) | C(5)-C(6) | 1.393(19) |
| N(1)-H1N() | 0.8800 | C(6)-H(6) | 0.9500 |
| C(1)-C(4) | 1.37(2) | | |

Symmetry transformations used to generate equivalent atoms:

(1) x-1,y,z (2) -x+2,-y+1,-z (3) x+1,y,z

Table S10. Bond angles [°] for (3-$BrCH_2PyH$)$PbBr_3$ at 173(2) K with estimated standard deviations in parentheses.

| Label | Angles | Label | Angles |
|---|---|---|---|
| Br(2)-Pb(1)-Br(3) | 89.81(4) | C(4)-C(1)-C(2) | 119.6(14) |
| Br(2)-Pb(1)-Br(2)#1 | 94.02(4) | C(4)-C(1)-H1C() | 120.2 |
| Br(3)-Pb(1)-Br(2)#1 | 96.53(4) | C(2)-C(1)-H1C() | 120.2 |
| Br(2)-Pb(1)-Br(1) | 89.86(4) | C(1)-C(2)-C(5) | 121.0(13) |
| Br(3)-Pb(1)-Br(1) | 90.92(4) | C(1)-C(2)-H(2) | 119.5 |
| Br(2)#1-Pb(1)-Br(1) | 171.61(4) | C(5)-C(2)-H(2) | 119.5 |
| Br(2)-Pb(1)-Br(1)#2 | 87.57(4) | C(5)-C(3)-Br(4) | 110.5(10) |
| Br(3)-Pb(1)-Br(1)#2 | 174.91(4) | C(5)-C(3)-H(3A) | 109.5 |
| Br(2)#1-Pb(1)-Br(1)#2 | 88.01(4) | Br(4)-C(3)-H(3A) | 109.5 |
| Br(1)-Pb(1)-Br(1)#2 | 84.71(4) | C(5)-C(3)-H(3AB) | 109.5 |
| Br(2)-Pb(1)-Br(1)#1 | 172.83(4) | Br(4)-C(3)-H(3AB) | 109.5 |
| Br(3)-Pb(1)-Br(1)#1 | 97.32(4) | H(3A)-C(3)-H(3AB) | 108.1 |
| Br(2)#1-Pb(1)-Br(1)#1 | 85.92(4) | N(1)-C(4)-C(1) | 118.7(14) |
| Br(1)-Pb(1)-Br(1)#1 | 89.31(4) | N(1)-C(4)-H(4) | 120.6 |
| Br(1)#2-Pb(1)-Br(1)#1 | 85.26(4) | C(1)-C(4)-H(4) | 120.6 |
| Pb(1)-Br(1)-Pb(1)#2 | 95.28(4) | C(2)-C(5)-C(6) | 117.9(13) |
| Pb(1)-Br(1)-Pb(1)#3 | 89.31(4) | C(2)-C(5)-C(3) | 123.6(12) |
| Pb(1)#2-Br(1)-Pb(1)#3 | 94.74(4) | C(6)-C(5)-C(3) | 118.5(13) |
| Pb(1)-Br(2)-Pb(1)#3 | 94.02(4) | N(1)-C(6)-C(5) | 119.3(13) |
| C(6)-N(1)-C(4) | 123.4(13) | N(1)-C(6)-H(6) | 120.4 |
| C(6)-N(1)-H1N() | 118.3 | C(5)-C(6)-H(6) | 120.4 |
| C(4)-N(1)-H1N() | 118.3 | | |

Symmetry transformations used to generate equivalent atoms:

(1) x-1,y,z (2) -x+2,-y+1,-z (3) x+1,y,z

Table S11. Crystal data and structure refinement for (4-$BrCH_2PyH)PbBr_3$ at 173(2) K.

| | |
|---|---|
| Empirical formula | C6 H7 Br4 N Pb |
| Formula weight | 619.96 |
| Temperature | 173(2) K |
| Wavelength | 0.71073 Å |
| Crystal system | monoclinic |
| Space group | $P2_1/c$ |
| Unit cell dimensions | a = 4.365(3) Å, α = 90°<br>b = 13.137(8) Å, β = 94.66(4)°<br>c = 20.534(12) Å, γ = 90° |
| Volume | 1173.4(13) $Å^3$ |
| Z | 4 |
| Density (calculated) | 3.509 $g/cm^3$ |
| Absorption coefficient | 27.950 $mm^{-1}$ |
| F(000) | 1088 |
| Crystal size | 0.121 x 0.056 x 0.052 $mm^3$ |
| θ range for data collection | 2.523 to 25.310° |
| Index ranges | -5<=h<=5, -15<=k<=15, -24<=l<=24 |
| Reflections collected | 10641 |
| Independent reflections | 2128 [$R_{int}$ = 0.0427] |
| Completeness to θ = 25.242° | 99.5% |
| Refinement method | Full-matrix least-squares on $F^2$ |
| Data / restraints / parameters | 2128 / 0 / 109 |
| Goodness-of-fit | 1.159 |
| Final R indices [I > 2σ(I)] | $R_{obs}$ = 0.0232, $wR_{obs}$ = 0.0593 |
| R indices [all data] | $R_{all}$ = 0.0257, $wR_{all}$ = 0.0605 |
| Extinction coefficient | . |
| Largest diff. peak and hole | 0.931 and -1.832 e·$Å^{-3}$ |

$R = \Sigma||F_o|-|F_c|| / \Sigma|F_o|$, $wR = \{\Sigma[w(|F_o|^2 - |F_c|^2)^2] / \Sigma[w(|F_o|^4)]\}^{1/2}$ and $w=1/[\sigma^2(Fo^2)+(0.0301P)^2+0.6925P]$

where $P=(Fo^2+2Fc^2)/3$

Table S12. Atomic coordinates ($x10^4$) and equivalent isotropic displacement parameters ($Å^2x10^3$) for (4-$BrCH_2PyH)PbBr_3$ at 173(2) K with estimated standard deviations in parentheses.

| Label | x | y | z | Occupancy | $U_{eq}$* |
|---|---|---|---|---|---|
| Pb(1) | 5946(1) | 8689(1) | 5599(1) | 1 | 17(1) |
| Br(1) | 10552(2) | 8874(1) | 4527(1) | 1 | 18(1) |
| Br(2) | 1199(2) | 8182(1) | 6562(1) | 1 | 20(1) |
| Br(3) | 6648(2) | 4159(1) | 1944(1) | 1 | 23(1) |
| Br(4) | 5639(2) | 6658(1) | 5243(1) | 1 | 19(1) |
| C(1) | 6509(14) | 6199(5) | 3060(3) | 1 | 24(2) |
| H(1) | 5205.07 | 6457.47 | 2705.48 | 1 | 29 |
| N(1) | 10042(11) | 6480(4) | 3957(2) | 1 | 20(2) |
| H(1A) | 11110.52 | 6909.21 | 4214.21 | 1 | 23 |
| C(2) | 8231(13) | 6851(5) | 3466(3) | 1 | 23(2) |
| H(2) | 8120.49 | 7565.22 | 3393.19 | 1 | 28 |
| C(3) | 6692(12) | 5162(5) | 3174(3) | 1 | 19(2) |
| C(4) | 4727(14) | 4437(6) | 2751(3) | 1 | 28(2) |
| H(4A) | 2666.75 | 4737.68 | 2646.57 | 1 | 34 |
| H(4AB) | 4470.16 | 3792.33 | 2990.8 | 1 | 34 |
| C(5) | 8660(12) | 4803(5) | 3688(3) | 1 | 19(2) |
| H(5) | 8855.23 | 4092.21 | 3767.59 | 1 | 23 |
| C(6) | 10326(13) | 5489(4) | 4081(3) | 1 | 19(2) |
| H(6) | 11667.31 | 5256.66 | 4437.23 | 1 | 23 |

*$U_{eq}$ is defined as one third of the trace of the orthogonalized $U_{ij}$ tensor.

Table S13. Anisotropic displacement parameters ($Å^2x10^3$) for (4-$BrCH_2PyH)PbBr_3$ at 173(2) K with estimated standard deviations in parentheses.

| Label | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{12}$ | $U_{13}$ | $U_{23}$ |
|---|---|---|---|---|---|---|
| Pb(1) | 20(1) | 15(1) | 16(1) | -2(1) | 0(1) | -1(1) |
| Br(1) | 26(1) | 14(1) | 14(1) | -1(1) | 2(1) | -1(1) |
| Br(2) | 21(1) | 25(1) | 14(1) | -1(1) | -1(1) | -1(1) |
| Br(3) | 24(1) | 26(1) | 18(1) | -4(1) | 2(1) | -8(1) |
| Br(4) | 21(1) | 14(1) | 20(1) | 0(1) | 0(1) | -1(1) |
| C(1) | 28(3) | 25(4) | 18(3) | 5(3) | -3(3) | 3(3) |
| N(1) | 27(3) | 17(3) | 15(2) | -3(2) | 1(2) | -7(2) |
| C(2) | 31(3) | 18(3) | 20(3) | 6(3) | -5(3) | 0(3) |
| C(3) | 16(3) | 26(3) | 15(3) | -1(2) | 6(2) | -7(2) |
| C(4) | 25(3) | 39(4) | 22(3) | -10(3) | 9(3) | -17(3) |
| C(5) | 23(3) | 15(3) | 19(3) | -1(2) | 6(2) | -1(2) |
| C(6) | 25(3) | 14(3) | 18(3) | 2(2) | -1(2) | 3(2) |

The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11} + ... + 2hka^*b^*U_{12}]$.

Table S14. Bond lengths [Å] for (4-$BrCH_2PyH$)$PbBr_3$ at 173(2) K with estimated standard deviations in parentheses.

| Label | Distances |
|---|---|
| Pb(1)-Br(4) | 2.7673(16) |
| Pb(1)-Br(2)#1 | 2.9787(18) |
| Pb(1)-Br(2) | 3.0512(17) |
| Pb(1)-Br(1)#2 | 3.0992(19) |
| Pb(1)-Br(1) | 3.1092(18) |
| Br(3)-C(4) | 1.951(6) |
| C(1)-C(2) | 1.375(9) |
| C(1)-C(3) | 1.383(9) |
| C(1)-H(1) | 0.9500 |
| N(1)-C(2) | 1.324(7) |
| N(1)-C(6) | 1.330(7) |
| N(1)-H(1A) | 0.8800 |
| C(2)-H(2) | 0.9500 |
| C(3)-C(5) | 1.389(8) |
| C(3)-C(4) | 1.509(8) |
| C(4)-H(4A) | 0.9900 |
| C(4)-H(4AB) | 0.9900 |
| C(5)-C(6) | 1.378(8) |
| C(5)-H(5) | 0.9500 |
| C(6)-H(6) | 0.9500 |

Symmetry transformations used to generate equivalent atoms:

(1) x+1,y,z (2) x-1,y,z

Table S15. Bond angles [°] for (4-$BrCH_2PyH$)$PbBr_3$ at 173(2) K with estimated standard deviations in parentheses.

| Label | Angles | Label | Angles |
|---|---|---|---|
| Br(4)-Pb(1)-Br(2)#1 | 88.73(3) | N(1)-C(2)-C(1) | 119.7(6) |
| Br(4)-Pb(1)-Br(2) | 86.56(3) | N(1)-C(2)-H(2) | 120.2 |
| Br(2)#1-Pb(1)-Br(2) | 92.74(5) | C(1)-C(2)-H(2) | 120.2 |
| Br(4)-Pb(1)-Br(1)#2 | 82.54(2) | C(1)-C(3)-C(5) | 119.1(6) |
| Br(2)#1-Pb(1)-Br(1)#2 | 171.214(19) | C(1)-C(3)-C(4) | 120.2(6) |
| Br(2)-Pb(1)-Br(1)#2 | 87.75(5) | C(5)-C(3)-C(4) | 120.7(6) |
| Br(4)-Pb(1)-Br(1) | 84.74(2) | C(3)-C(4)-Br(3) | 110.1(4) |
| Br(2)#1-Pb(1)-Br(1) | 88.87(5) | C(3)-C(4)-H(4A) | 109.6 |
| Br(2)-Pb(1)-Br(1) | 171.111(18) | Br(3)-C(4)-H(4A) | 109.6 |
| Br(1)#2-Pb(1)-Br(1) | 89.34(5) | C(3)-C(4)-H(4AB) | 109.6 |
| Pb(1)#1-Br(1)-Pb(1) | 89.34(5) | Br(3)-C(4)-H(4AB) | 109.6 |
| Pb(1)#2-Br(2)-Pb(1) | 92.74(5) | H(4A)-C(4)-H(4AB) | 108.2 |
| C(2)-C(1)-C(3) | 119.4(6) | C(6)-C(5)-C(3) | 119.1(6) |
| C(2)-C(1)-H(1) | 120.3 | C(6)-C(5)-H(5) | 120.4 |
| C(3)-C(1)-H(1) | 120.3 | C(3)-C(5)-H(5) | 120.4 |
| C(2)-N(1)-C(6) | 123.2(5) | N(1)-C(6)-C(5) | 119.5(5) |
| C(2)-N(1)-H(1A) | 118.4 | N(1)-C(6)-H(6) | 120.2 |
| C(6)-N(1)-H(1A) | 118.4 | C(5)-C(6)-H(6) | 120.2 |

Symmetry transformations used to generate equivalent atoms:

(1) x+1,y,z (2) x-1,y,z

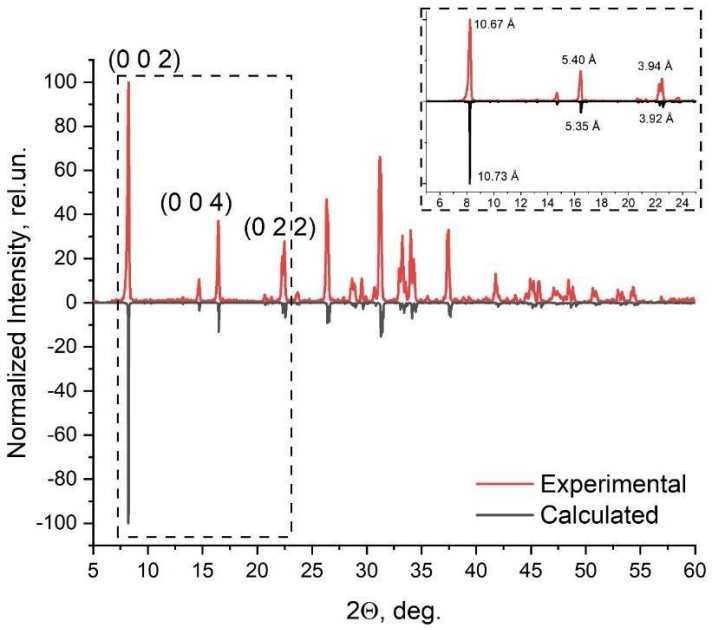


Figure S5. Experimental powder vs. simulated single crystal XRD patterns of (2-$BrCH_2PyH)Pb_2Br_5$. Inset: interplanar distances within the angle □ diffraction region [7.5-22.5]°.

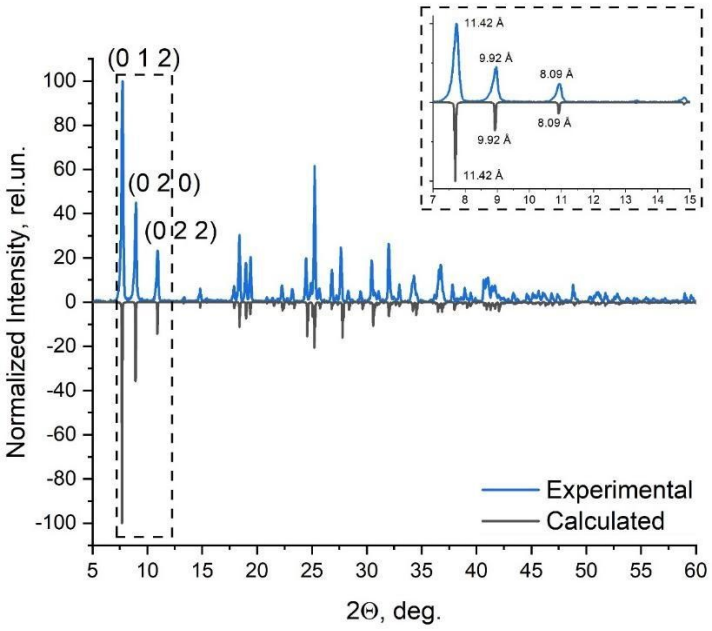


Figure S6. Experimental powder vs. simulated single crystal XRD patterns of (3-$BrCH_2PyH)PbBr_3$. Inset: interplanar distances within the angle □ diffraction region [7.5-12.5]°.

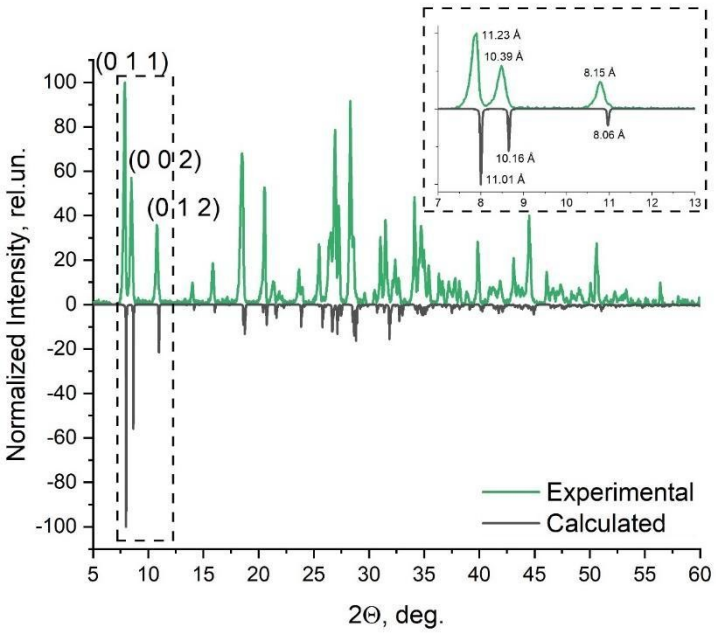


Figure S7. Experimental powder vs. simulated single crystal XRD patterns of (4-$BrCH_2PyH)PbBr_3$. Inset: interplanar distances within the angle □ diffraction region [7.5-22.5]°.

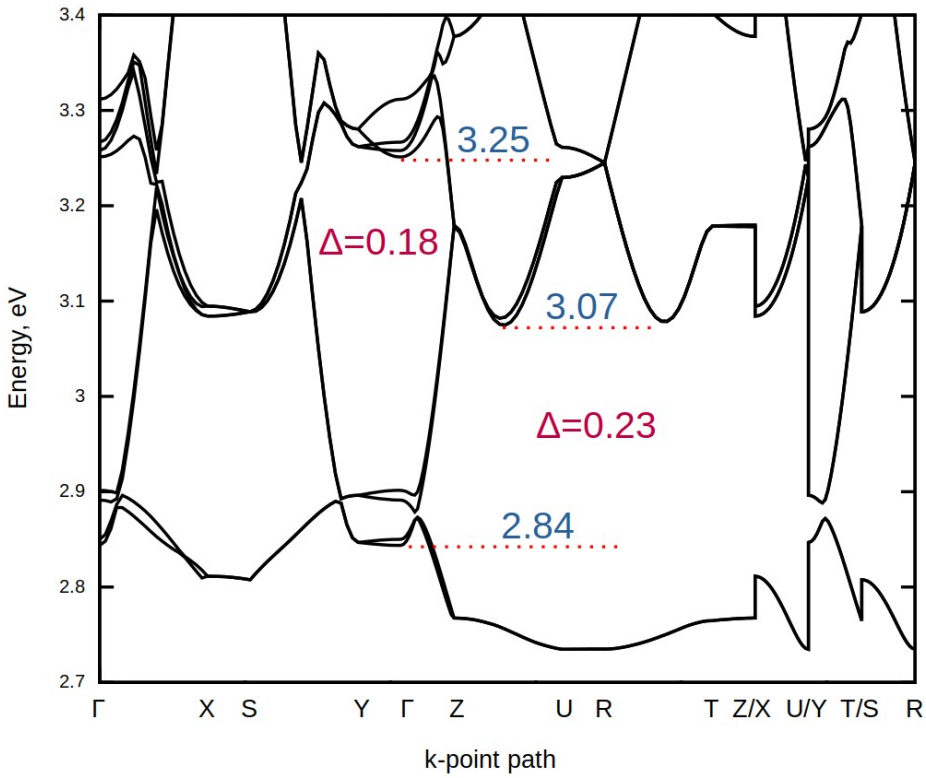


Figure S8. Unoccupied electronic bands in 2-(Bromomethyl)pyridinim lead bromide.

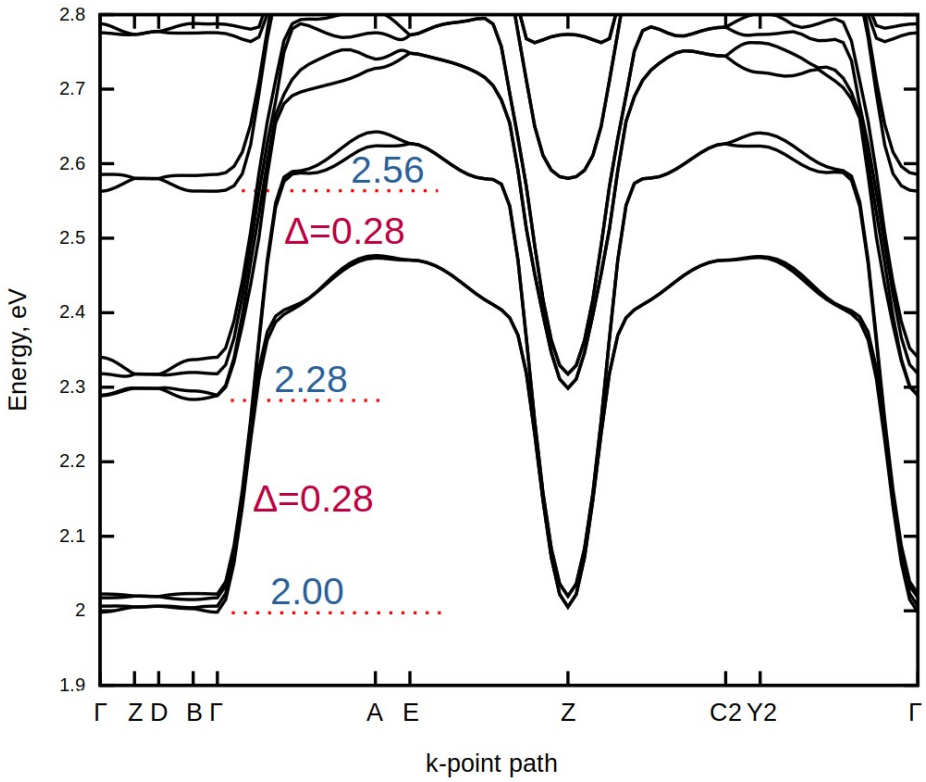


Figure S9. Unoccupied electronic bands in 3-(Bromomethyl)pyridinim lead bromide.

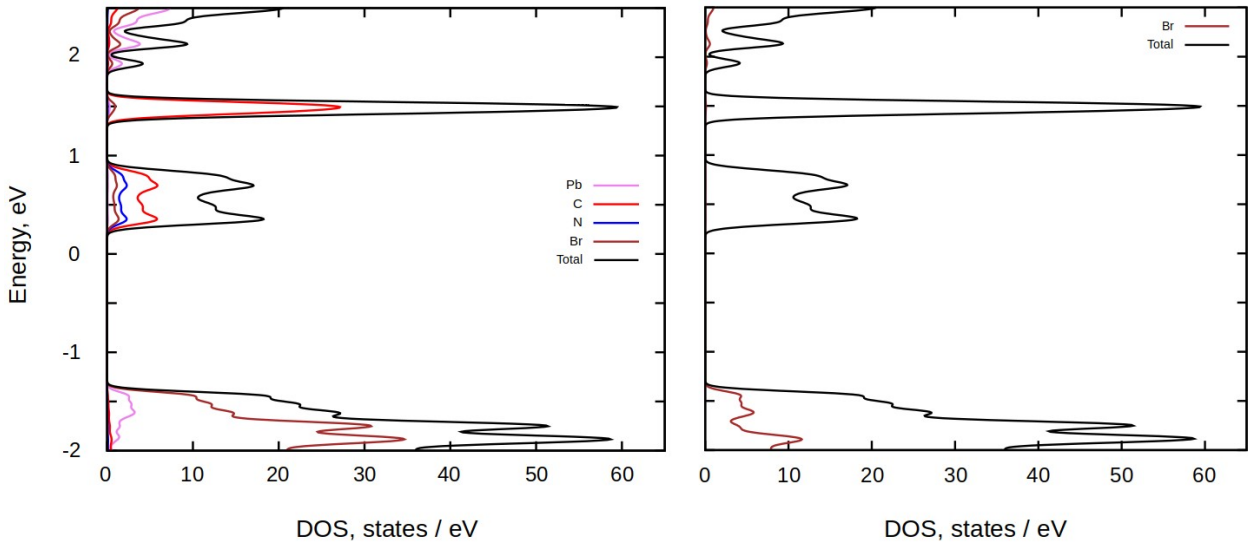

Figure S10. PDOS from all atoms (left) vs. PDOS from bromine atoms of the organic cations (right) in 4-(Bromomethyl)pyridinim lead bromide.