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Electronic Supplementary Information

The *N,N,N*-trimethylammonium moiety as tetrel bond donor site: crystallographic and computational studies

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S.1. Materials and Methods.

S.1.1. Materials.

Compounds and solvents were purchased from Sigma Aldrich and TCI and used without further purification.

S.1.2. Methods.

The single crystal data of all the structures displayed in this work were collected at Bruker SMART APEX II CCD area detector diffractometer at 100 K. Data collection, unit cell refinement and data reduction were performed using Bruker SAINT. The structure was solved by direct methods using SHELXT and refined by full-matrix least-squares on F^2 with anisotropic displacement parameters for the non-H atoms using SHELXL-2016/6. Absorption correction was performed based on multi-scan procedure using SADABS. Structure analysis was aided by use of the programs PLATON. The hydrogen atoms were calculated in ideal positions with isotropic displacement parameters set to 1.2xUeq of the attached atom.

S.2. Crystallographic Details.

S.2.1. Parameters and data for X-Ray crystal structures 1-5 refined by IAM.

Table S.1. Crystal data and structure refinement for **1**[1].

Identification code	**1**
Empirical formula	$C_{12}H_{30}Br_2N_2$
Formula weight	362.20
Temperature/K	93(2)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	5.4796(4)
b/Å	13.1109(11)
c/Å	11.5815(9)
α/°	90.00
β/°	93.580(4)
γ/°	90.00
Volume/Å^3	830.42(11)
Z	2
ρ_{calc}g/cm^3	1.449
μ/mm^{-1}	4.864
F(000)	372.0
Crystal size/mm^3	0.12 × 0.1 × 0.06
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	6.22 to 65.58
Index ranges	-5 ≤ h ≤ 8, -18 ≤ k ≤ 19, -17 ≤ l ≤ 13
Reflections collected	13885
Independent reflections	2897 [R_{int} = 0.0397, R_{sigma} = 0.0365]
Data/restraints/parameters	2897/0/118
Goodness-of-fit on F^2	1.005
Final R indexes [I>=2σ (I)]	R_1 = 0.0235, wR_2 = 0.0441
Final R indexes [all data]	R_1 = 0.0408, wR_2 = 0.0481
CCDC Number	952024

Table S.2. Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for **1**. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
Br1	3771.2(3)	1031.33(11)	1853.34(12)	14.66(5)
N1	9751(2)	3226.0(9)	3806.0(10)	11.1(2)
C1	11017(3)	2269.5(11)	4266.7(13)	13.1(3)
C2	9325(3)	1368.5(11)	4424.0(14)	15.6(3)
C4	8058(3)	3626.1(12)	4661.8(13)	14.2(3)
C5	11672(3)	4016.0(12)	3624.1(14)	15.0(3)
C6	8386(3)	3034.8(13)	2669.0(13)	16.9(3)
C3	10798(3)	466.7(11)	4918.9(14)	16.7(3)

Table S.3. Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for **1**. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Br1	14.82(7)	15.39(7)	13.75(7)	-3.67(6)	0.73(5)	-1.89(6)
N1	11.2(5)	10.5(5)	11.7(5)	0.0(4)	0.7(4)	0.6(4)
C1	15.6(7)	9.4(6)	14.0(7)	0.7(5)	-0.1(5)	2.2(5)
C2	19.7(7)	10.4(6)	16.2(7)	0.3(5)	-1.5(6)	-0.7(5)
C4	14.9(7)	12.5(6)	15.6(7)	-0.2(5)	2.9(5)	3.6(5)
C5	14.2(6)	12.8(6)	18.1(7)	1.6(6)	0.8(5)	-3.3(6)
C6	19.5(7)	15.9(7)	14.5(7)	0.4(6)	-4.6(6)	-2.2(6)
C3	20.8(8)	11.0(7)	18.2(7)	1.0(5)	0.7(6)	1.8(5)

Table S.4. Bond Lengths for **1**.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
N1	C1	1.5142(17)	C1	C2	1.520(2)
N1	C4	1.4943(18)	C2	C3	1.523(2)
N1	C5	1.5009(18)	C3	C3[1]	1.523(3)
N1	C6	1.4943(18)			

[1]2-X,-Y,1-Z

Table S.5. Bond Angles for **1**.

Atom	Atom	Atom	Angle/˚	Atom	Atom	Atom	Angle/˚
C4	N1	C1	110.30(11)	C6	N1	C5	107.99(11)
C4	N1	C5	108.71(11)	N1	C1	C2	114.60(12)
C4	N1	C6	110.26(12)	C1	C2	C3	109.59(12)
C5	N1	C1	108.12(11)	C3[1]	C3	C2	112.03(16)
C6	N1	C1	111.38(11)				

[1]2-X,-Y,1-Z

Table S.6. Torsion Angles for **1**.

A	B	C	D	Angle/˚	A	B	C	D	Angle/˚
N1	C1	C2	C3	-178.52(12)	C5	N1	C1	C2	-176.21(12)
C1	C2	C3	C3[1]	-179.23(16)	C6	N1	C1	C2	-57.72(16)
C4	N1	C1	C2	65.05(15)					

[1]2-X,-Y,1-Z

Table S.7. Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for **1**.

Atom	*x*	*y*	*z*	U(eq)
H1A	11850(30)	2501(13)	4999(15)	16
H1B	12180(30)	2077(13)	3713(14)	16
H2A	8550(30)	1148(13)	3693(17)	19
H2B	8010(30)	1543(14)	4957(15)	19
H4A	6760(30)	3130(14)	4805(15)	21
H4B	7350(30)	4211(14)	4353(17)	21
H4C	8910(30)	3712(13)	5387(17)	21
H5A	12550(30)	4154(13)	4341(17)	23
H5B	10890(30)	4627(15)	3350(15)	23
H5C	12720(30)	3787(13)	3077(16)	23
H6A	7120(40)	2587(14)	2748(17)	25
H6B	9520(30)	2748(15)	2165(16)	25
H6C	7810(30)	3650(14)	2384(17)	25
H3A	11670(30)	659(13)	5640(16)	20
H3B	12100(30)	298(13)	4375(15)	20

Table S.8. Crystal data and structure refinement for **2²**.

Identification code	**2**
Empirical formula	$C_{12}H_{34}N_2O_2Br_2$
Formula weight	398.22
Temperature/K	103.15
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	7.3339(13)
b/Å	18.292(3)
c/Å	7.0915(12)
α/°	90
β/°	108.824(4)
γ/°	90
Volume/Å^3	900.4(3)
Z	2
ρ_{calc}g/cm^3	1.4687
μ/mm^{-1}	4.500
F(000)	411.1
Crystal size/mm^3	0.32 × 0.16 × 0.06
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	5.86 to 60.48
Index ranges	-10 ≤ h ≤ 10, -25 ≤ k ≤ 25, -7 ≤ l ≤ 9
Reflections collected	30774
Independent reflections	2604 [R_{int} = 0.0286, R_{sigma} = 0.0146]
Data/restraints/parameters	2604/0/93
Goodness-of-fit on F^2	1.040
Final R indexes [I>=2σ (I)]	R_1 = 0.0172, wR_2 = 0.0424
Final R indexes [all data]	R_1 = 0.0200, wR_2 = 0.0439
CCDC Number	797580

Table S.9. Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for **2**. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
Br1	3088.09(16)	3671.69(6)	1674.07(18)	15.06(4)
N1	6417.6(15)	1255.5(5)	2836.2(16)	12.08(19)
C1	7639.3(18)	1194.4(7)	1476.7(18)	13.3(2)
C2	8839.6(17)	499.4(7)	1757.6(18)	13.7(2)
C3	9423.8(17)	352.9(6)	-89.3(18)	13.3(2)
C4	5515(2)	1999.5(7)	2551(2)	19.5(3)
C5	7617.2(19)	1165.8(8)	4975.3(19)	20.5(3)
C6	4836.8(18)	698.4(7)	2306(2)	17.2(2)
O1	354.1(18)	2275.2(7)	9008(2)	37.2(3)

Table S.10. Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for **2**. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Br1	15.15(6)	14.48(6)	16.07(7)	0.57(4)	5.76(5)	-0.90(4)
N1	12.6(4)	12.7(4)	11.7(4)	1.0(3)	4.9(4)	-0.7(4)
C1	14.5(5)	13.6(5)	13.8(5)	1.5(4)	7.6(4)	0.6(4)
C2	15.0(5)	13.8(5)	13.3(5)	2.8(4)	6.1(4)	1.0(4)
C3	14.8(5)	13.2(5)	13.5(5)	1.0(4)	6.7(4)	0.8(4)
C4	24.0(6)	13.4(5)	24.3(6)	5.9(5)	12.1(5)	0.5(5)
C5	16.8(6)	33.4(7)	10.5(5)	3.2(5)	3.3(4)	-0.0(5)
C6	15.6(5)	17.0(6)	20.6(6)	-3.5(5)	8.1(5)	-2.8(5)
O1	29.6(6)	34.8(6)	47.2(7)	-2.5(5)	12.6(5)	-11.3(6)

Table S.11. Bond Lengths for **2**.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
N1	C1	1.5174(15)	C1	C2	1.5223(16)
N1	C4	1.4982(16)	C2	C3	1.5274(17)
N1	C5	1.4969(16)	C3	C3[1]	1.526(2)
N1	C6	1.4975(16)			

[1]2-X,-Y,-Z

Table S.12. Bond Angles for **2**.

Atom	Atom	Atom	Angle/˚	Atom	Atom	Atom	Angle/˚
C4	N1	C1	107.86(9)	C6	N1	C5	109.52(10)
C5	N1	C1	111.18(10)	C2	C1	N1	114.42(10)
C5	N1	C4	109.02(10)	C3	C2	C1	110.16(9)
C6	N1	C1	111.00(9)	C3[1]	C3	C2	112.24(12)
C6	N1	C4	108.17(10)				

[1]2-X,-Y,-Z

Table S.13. Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for **2**.

Atom	*x*	*y*	*z*	U(eq)
H1a	6781.8(18)	1217.3(7)	76.6(18)	15.9(3)
H1b	8514.9(18)	1621.0(7)	1710.1(18)	15.9(3)
H2a	10007.4(17)	551.8(7)	2937.1(18)	16.4(3)
H2b	8083.6(17)	81.1(7)	1992.4(18)	16.4(3)
H3a	8250.8(17)	321.6(6)	-1270.6(18)	16.0(3)
H3b	10207.1(17)	767.5(6)	-294.3(18)	16.0(3)
H4a	4749(13)	2066(2)	1147(4)	29.3(4)
H4b	4679(13)	2047(2)	3379(13)	29.3(4)
H4c	6527(2)	2372.7(7)	2940(16)	29.3(4)
H5a	6820(4)	1256(6)	5826(2)	30.8(4)
H5b	8130(13)	667(2)	5195(4)	30.8(4)
H5c	8686(9)	1516(4)	5305(5)	30.8(4)
H6a	4023(9)	768(4)	3150(11)	25.8(3)
H6b	4055(9)	756(4)	904(5)	25.8(3)
H6c	5397.6(18)	206.8(7)	2518(15)	25.8(3)
H1c	1320(40)	2644(15)	9840(40)	71(8)
H1d	1320(50)	2030(20)	8230(50)	127(13)

Table S.14. Crystal data and structure refinement for **3**.

Identification code	**3**
Empirical formula	$C_{13}H_{34}N_2Br_2O$
Formula weight	394.24
Temperature/K	93(2)
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	9.270(2)
b/Å	11.720(3)
c/Å	16.537(4)
α/°	90.00
β/°	92.20(3)
γ/°	90.00
Volume/Å^3	1795.3(7)
Z	4
ρ_{calc}g/cm^3	1.459
μ/mm^{-1}	4.510
F(000)	816.0
Crystal size/mm^3	0.32 × 0.05 × 0.01
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.26 to 50.06
Index ranges	-10 ≤ h ≤ 11, -13 ≤ k ≤ 13, -19 ≤ l ≤ 19
Reflections collected	14875
Independent reflections	3154 [R_{int} = 0.1308, R_{sigma} = 0.1329]
Data/restraints/parameters	3154/0/171
Goodness-of-fit on F^2	0.953
Final R indexes [I>=2σ (I)]	R_1 = 0.0503, wR_2 = 0.0894
Final R indexes [all data]	R_1 = 0.1293, wR_2 = 0.1117
CCDC Number	2118170

Table S.15. Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for **3**. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	*X*	*y*	*z*	U(eq)
Br1	7452.6(7)	5728.1(6)	1146.8(4)	23.6(2)
Br2	2853.4(8)	-597.2(6)	1123.9(4)	24.8(2)
N1	2053(6)	5732(5)	1140(3)	20.2(13)
N2	-1663(6)	-684(5)	1589(3)	19.4(13)
C1	1322(8)	4584(6)	990(4)	23.7(18)
C2	1780(8)	3631(6)	1575(4)	24.1(18)
C3	948(8)	2523(6)	1344(4)	26.0(19)
C4	-588(8)	2529(6)	1603(4)	26.5(19)
C5	-1484(8)	1481(6)	1315(4)	22.2(18)
C6	-932(7)	437(6)	1796(4)	23.9(18)
C7	3639(8)	5659(6)	1087(4)	29.7(18)
C8	1471(8)	6521(6)	494(4)	26.1(19)
C9	1648(8)	6209(6)	1944(4)	28.1(19)
C10	-1272(8)	-1086(6)	760(4)	26.6(19)
C11	-1110(8)	-1529(6)	2196(4)	27.7(19)
C12	-3266(7)	-614(7)	1620(4)	25.2(17)
C13	4884(8)	2366(7)	575(4)	37(2)
O1	4689(6)	1849(4)	1349(3)	30.8(13)

Table S.16. Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for **3**. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Br1	28.7(5)	26.6(4)	15.6(4)	-0.5(4)	1.9(3)	-0.2(4)
Br2	30.9(5)	25.9(4)	17.4(4)	-2.1(4)	-0.7(3)	0.1(4)
N1	22(4)	22(3)	17(3)	-1(3)	-4(2)	0(3)
N2	28(4)	17(3)	13(3)	1(3)	3(2)	-1(3)
C1	33(5)	28(5)	10(4)	0(3)	-1(3)	-1(4)
C2	29(5)	21(5)	22(4)	0(3)	1(3)	3(3)
C3	42(6)	23(5)	12(4)	-1(3)	2(3)	1(4)
C4	34(5)	19(4)	27(4)	11(3)	5(3)	-2(3)
C5	19(5)	28(5)	20(4)	-2(3)	-1(3)	0(3)
C6	28(5)	25(5)	19(4)	0(3)	-3(3)	-4(3)
C7	40(5)	27(5)	22(4)	3(4)	-2(3)	0(4)
C8	36(5)	28(5)	14(4)	4(3)	-6(3)	3(4)
C9	44(6)	23(4)	17(4)	-8(3)	2(4)	-1(4)
C10	41(5)	22(4)	18(4)	-3(3)	4(4)	6(3)
C11	42(6)	22(5)	19(4)	2(3)	1(3)	5(4)
C12	29(5)	31(5)	15(4)	2(4)	3(3)	1(4)
C13	46(6)	46(6)	19(4)	4(4)	7(4)	-3(4)
O1	41(4)	29(3)	22(3)	2(2)	0(2)	-2(3)

Table S.17. Bond Lengths for **3**.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
N1	C1	1.522(8)	N2	C12	1.491(8)
N1	C7	1.479(8)	C1	C2	1.526(9)
N1	C8	1.497(8)	C2	C3	1.551(9)
N1	C9	1.503(8)	C3	C4	1.503(9)
N2	C6	1.511(8)	C4	C5	1.548(9)
N2	C10	1.508(8)	C5	C6	1.537(9)
N2	C11	1.487(8)	C13	O1	1.435(7)

Table S.18. Bond Angles for **3**.

Atom	Atom	Atom	Angle/˚	Atom	Atom	Atom	Angle/˚
C7	N1	C1	112.1(6)	C11	N2	C12	109.3(5)
C7	N1	C8	109.0(5)	C12	N2	C6	112.5(5)
C7	N1	C9	110.9(5)	C12	N2	C10	108.8(5)
C8	N1	C1	106.5(5)	N1	C1	C2	115.7(6)
C8	N1	C9	107.8(5)	C1	C2	C3	109.5(6)
C9	N1	C1	110.3(5)	C4	C3	C2	113.2(6)
C10	N2	C6	110.9(5)	C3	C4	C5	114.3(6)
C11	N2	C6	106.7(5)	C6	C5	C4	107.9(6)
C11	N2	C10	108.5(5)	N2	C6	C5	115.9(6)

Table S.19. Torsion Angles for **3**.

A	B	C	D	Angle/˚	A	B	C	D	Angle/˚
N1	C1	C2	C3	-179.9(6)	C8	N1	C1	C2	178.9(6)
C1	C2	C3	C4	-76.8(7)	C9	N1	C1	C2	-64.4(7)
C2	C3	C4	C5	174.9(6)	C10	N2	C6	C5	69.7(7)
C3	C4	C5	C6	70.9(7)	C11	N2	C6	C5	-172.4(5)
C4	C5	C6	N2	-179.0(6)	C12	N2	C6	C5	-52.5(7)
C7	N1	C1	C2	59.7(7)					

Table S.20. Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for **3**.

Atom	*x*	*y*	*z*	U(eq)
H1A	1519	4336	439	28
H1B	277	4690	1018	28
H2A	1571	3853	2129	29
H2B	2821	3499	1549	29
H3A	954	2421	756	31
H3B	1452	1871	1595	31
H4A	-1062	3222	1393	32
H4B	-587	2564	2195	32
H5A	-2510	1607	1408	27
H5B	-1373	1357	734	27
H6A	103	354	1712	29
H6B	-1046	589	2373	29
H7A	4057	6412	1161	45
H7B	3876	5365	560	45
H7C	4024	5152	1506	45
H8A	429	6564	520	39
H8B	1724	6235	-32	39
H8C	1883	7275	577	39
H9A	2020	5716	2374	42
H9B	605	6253	1964	42
H9C	2057	6966	2012	42
H10A	-1700	-579	353	40
H10B	-1633	-1854	671	40
H10C	-230	-1082	721	40
H11A	-63	-1529	2210	42
H11B	-1464	-2283	2049	42
H11C	-1444	-1326	2726	42
H12A	-3531	-394	2160	38
H12B	-3684	-1353	1487	38
H12C	-3627	-51	1233	38
H13A	3951	2577	334	55
H13B	5353	1829	224	55
H13C	5479	3043	642	55
H1	4183	1268	1291	46

Table S.21. Crystal data and structure refinement for **4**.

Identification code	**4**
Empirical formula	$C_{14}H_{33}N_3Br_2$
Formula weight	403.25
Temperature/K	103(2)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	12.4309(10)
b/Å	9.5074(8)
c/Å	15.9984(13)
α/°	90.00
β/°	94.584(5)
γ/°	90.00
Volume/Å^3	1884.7(3)
Z	4
ρ_{calc}g/cm^3	1.421
μ/mm^{-1}	4.296
F(000)	832.0
Crystal size/mm^3	0.62 × 0.2 × 0.18
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.98 to 69.44
Index ranges	-19 ≤ h ≤ 19, -14 ≤ k ≤ 14, -25 ≤ l ≤ 25
Reflections collected	44615
Independent reflections	6920 [R_{int} = 0.0610, R_{sigma} = 0.0474]
Data/restraints/parameters	6920/0/180
Goodness-of-fit on F^2	1.112
Final R indexes [I>=2σ (I)]	R_1 = 0.0503, wR_2 = 0.1438
Final R indexes [all data]	R_1 = 0.0684, wR_2 = 0.1519
CCDC Number	952025

Table S.22. Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for **4**. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	*X*	*y*	*z*	U(eq)
Br1	837.2(3)	2795.5(5)	1098.9(2)	15.72(10)
Br2	3900.8(4)	7767.8(5)	1210.9(2)	17.89(10)
N1	4277(3)	2462(3)	1211(2)	10.8(6)
N2	10642(3)	-1851(3)	1535.5(19)	11.4(6)
C1	5487(4)	2368(4)	1231(3)	15.3(7)
C6	7132(3)	880(4)	1259(2)	14.7(7)
C2	5963(3)	926(4)	1458(3)	16.3(7)
C4	8872(3)	-507(4)	1276(2)	14.8(7)
C5	9417(3)	-1880(4)	1548(2)	14.5(7)
C11	11025(4)	-3324(5)	1647(3)	20.2(8)
C7	3749(4)	1688(5)	465(2)	18.7(8)
C8	3989(4)	3990(5)	1130(3)	27.2(10)
C10	11157(4)	-959(5)	2226(2)	17.7(8)
C9	3850(3)	1876(5)	1995(2)	17.2(8)
C3	7713(3)	-457(4)	1549(2)	13.3(7)
C12	10969(3)	-1314(4)	710(2)	14.2(7)
N3	2979(4)	10679(5)	3587(2)	29.6(9)
C13	2504(3)	10120(5)	4080(2)	18.0(8)
C14	1912(4)	9398(5)	4698(2)	19.4(8)

Table S.23. Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for **4**. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Br1	13.4(2)	13.96(18)	19.79(16)	-0.46(16)	1.18(14)	0.27(17)
Br2	14.1(2)	14.40(19)	24.65(18)	1.33(17)	-1.38(15)	-0.06(17)
N1	3.3(14)	7.3(15)	22.4(14)	2.9(11)	3.6(11)	1.0(11)
N2	10.6(15)	9.5(14)	13.9(12)	1.0(11)	-0.1(10)	-0.9(11)
C1	12.7(18)	10.7(17)	22.0(16)	-1.5(14)	-2.2(14)	-0.4(15)
C6	8.1(17)	13.6(18)	21.7(17)	1.6(15)	-2.8(13)	-3.9(15)
C2	11.8(18)	12.2(17)	24.7(18)	0.9(14)	0.6(15)	0.1(16)
C4	10.3(17)	17.9(18)	16.2(15)	2.5(13)	0.8(13)	2.0(16)
C5	10.8(17)	13.1(17)	19.8(16)	2.8(13)	2.7(14)	-1.7(15)
C11	14.3(19)	14.1(19)	32(2)	8.2(17)	2.9(16)	0.1(17)
C7	13.7(18)	21(2)	21.0(17)	-4.3(15)	-1.5(15)	2.8(17)
C8	27(3)	13(2)	42(3)	3.3(18)	5(2)	4.3(19)
C10	17(2)	18.2(19)	17.0(16)	-0.7(14)	-4.3(14)	-2.4(16)
C9	9.6(17)	23(2)	18.8(16)	1.6(14)	2.2(13)	3.0(16)
C3	8.2(18)	14.5(18)	17.4(15)	1.0(14)	1.7(13)	-0.6(14)
C12	9.3(17)	20.4(19)	13.2(15)	0.7(14)	2.8(12)	1.1(15)
N3	31(2)	35(2)	23.2(18)	1.0(17)	5.0(17)	-4(2)
C13	16(2)	22(2)	16.2(16)	-2.2(15)	-0.9(14)	2.8(18)
C14	19(2)	18.2(19)	20.9(17)	0.5(15)	3.7(15)	-3.4(17)

Table S.24. Bond Lengths for **4**.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
N1	C1	1.504(5)	C1	C2	1.526(6)
N1	C7	1.508(5)	C6	C2	1.513(6)
N1	C8	1.499(5)	C6	C3	1.516(6)
N1	C9	1.507(5)	C4	C5	1.518(6)
N2	C5	1.525(5)	C4	C3	1.539(5)
N2	C11	1.485(5)	N3	C13	1.151(6)
N2	C10	1.495(5)	C13	C14	1.451(6)
N2	C12	1.501(5)			

Table S.25. Bond Angles for **4**.

Atom	Atom	Atom	Angle/˚	Atom	Atom	Atom	Angle/˚
C1	N1	C7	111.1(3)	C10	N2	C12	109.1(3)
C1	N1	C9	112.2(3)	C12	N2	C5	111.0(3)
C8	N1	C1	106.9(3)	N1	C1	C2	115.3(3)
C8	N1	C7	108.6(3)	C2	C6	C3	113.7(3)
C8	N1	C9	109.4(3)	C6	C2	C1	109.7(4)
C9	N1	C7	108.6(3)	C5	C4	C3	110.6(3)
C11	N2	C5	107.0(3)	C4	C5	N2	113.9(3)
C11	N2	C10	109.4(3)	C6	C3	C4	111.9(3)
C11	N2	C12	108.6(3)	N3	C13	C14	179.3(5)
C10	N2	C5	111.7(3)				

Table S.26. Torsion Angles for **4**.

A	B	C	D	Angle/˚	A	B	C	D	Angle/˚
N1	C1	C2	C6	166.7(3)	C10	N2	C5	C4	71.5(4)
C2	C6	C3	C4	175.8(3)	C9	N1	C1	C2	50.2(4)
C5	C4	C3	C6	-178.0(3)	C3	C6	C2	C1	173.8(3)
C11	N2	C5	C4	-168.9(3)	C3	C4	C5	N2	-163.2(3)
C7	N1	C1	C2	-71.5(4)	C12	N2	C5	C4	-50.5(4)
C8	N1	C1	C2	170.2(3)					

Table S.27. Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for **4**.

Atom	*x*	*y*	*z*	U(eq)
H1A	5802	3063	1642	18
H1B	5710	2638	673	18
H6A	7516	1695	1528	18
H6B	7165	974	645	18
H2A	5913	742	2063	20
H2B	5549	188	1137	20
H4A	8855	-417	659	18
H4B	9291	292	1530	18
H5A	9126	-2641	1173	17
H5B	9232	-2106	2123	17
H11A	10702	-3905	1187	30
H11B	10812	-3690	2182	30
H11C	11813	-3350	1645	30
H7A	4019	2058	-50	28
H7B	2965	1818	444	28
H7C	3918	683	515	28
H8A	4250	4365	613	41
H8B	4325	4506	1612	41
H8C	3203	4096	1111	41
H10A	10908	-1263	2763	26
H10B	10958	27	2125	26
H10C	11944	-1056	2243	26
H9A	3079	2091	1996	26
H9B	4239	2302	2488	26
H9C	3954	855	2011	26
H3A	7305	-1280	1313	16
H3B	7735	-518	2167	16
H12A	11752	-1412	692	21
H12B	10769	-321	647	21
H12C	10600	-1860	253	21
H14A	2406	8797	5045	29
H14B	1343	8819	4411	29
H14C	1585	10092	5053	29

Table S.28. Crystal data and structure refinement for **5**.

Identification code	**5**
Empirical formula	$C_{14}H_{33}N_3I_2$
Formula weight	497.23
Temperature/K	103(2)
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	9.920(2)
b/Å	12.776(2)
c/Å	16.440(3)
α/°	90.00
β/°	96.07(2)
γ/°	90.00
Volume/Å^3	2071.9(7)
Z	4
ρ_{calc}g/cm^3	1.594
μ/mm^{-1}	3.031
F(000)	976.0
Crystal size/mm^3	0.14 × 0.08 × 0.04
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.04 to 61.02
Index ranges	-13 ≤ h ≤ 14, -17 ≤ k ≤ 18, -23 ≤ l ≤ 23
Reflections collected	21599
Independent reflections	6177 [R_{int} = 0.0489, R_{sigma} = 0.0631]
Data/restraints/parameters	6177/0/173
Goodness-of-fit on F^2	0.973
Final R indexes [I>=2σ (I)]	R_1 = 0.0372, wR_2 = 0.0607
Final R indexes [all data]	R_1 = 0.0703, wR_2 = 0.0686
CCDC Number	952023

Table S.29 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for **5**. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
I1	7314.6(2)	793.36(18)	1216.51(13)	21.80(6)
I2	2389.1(2)	3749.47(18)	1114.33(13)	23.35(7)
N1	7712(3)	4226(2)	1280.3(16)	22.4(7)
N2	12043(3)	10351(2)	1403.4(15)	18.0(6)
C1	7829(3)	5406(3)	1327(2)	23.9(8)
C2	9238(4)	5845(3)	1284(2)	26.3(8)
C3	9226(4)	7025(3)	1426(2)	25.1(8)
C4	10586(4)	7537(3)	1353(2)	26.7(8)
C5	10585(4)	8713(3)	1487(2)	23.9(8)
C6	11969(3)	9170(3)	1409(2)	21.6(7)
C7	13518(3)	10641(3)	1410(2)	29.0(9)
C8	11500(4)	10831(3)	2135.3(18)	23.6(8)
C9	11278(3)	10798(3)	645.6(18)	22.4(8)
C10	8523(4)	3721(3)	2001(2)	29.6(9)
C11	6246(4)	3965(3)	1304(3)	37.9(10)
C12	8167(4)	3808(3)	508(2)	28.6(9)
N3	5411(5)	2986(4)	8513(3)	79.9(15)
C13	4953(4)	2522(3)	8997(2)	35.6(10)
C14	4381(4)	1929(3)	9622(2)	30.5(9)

Table S.30. Anisotropic Displacement Parameters (Å^2×10^3) for **5**. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
I1	19.65(13)	19.40(12)	26.53(11)	0.88(9)	3.27(9)	-1.22(10)
I2	23.85(14)	20.28(13)	25.88(11)	-2.79(9)	2.48(9)	-1.57(11)
N1	27.0(18)	16.0(15)	24.6(14)	-1.1(11)	4.9(13)	-7.4(13)
N2	16.3(15)	17.8(15)	19.5(13)	0.2(11)	-0.8(11)	-4.0(13)
C1	29(2)	13.6(17)	29.8(18)	-0.5(14)	7.1(16)	-2.5(16)
C2	28(2)	18.8(19)	32.1(18)	-0.6(15)	2.6(16)	-4.6(17)
C3	25(2)	16.9(19)	33.4(18)	-0.2(15)	4.5(16)	-3.5(16)
C4	24(2)	18.3(19)	37(2)	-1.9(16)	0.8(17)	-0.3(16)
C5	24(2)	17.8(18)	30.7(17)	-1.0(15)	5.8(15)	-0.1(16)
C6	25(2)	15.2(17)	24.9(16)	-0.6(14)	2.6(14)	-0.4(16)
C7	17(2)	32(2)	38(2)	-2.9(16)	0.5(16)	-7.2(17)
C8	32(2)	18.8(18)	20.9(15)	-2.5(14)	5.0(15)	-3.6(16)
C9	25(2)	22.8(19)	18.2(15)	0.2(14)	-1.0(14)	-1.3(16)
C10	45(3)	19.8(19)	23.6(17)	2.3(15)	3.7(17)	-4.0(18)
C11	24(2)	31(2)	60(3)	-4(2)	13(2)	-7.9(19)
C12	36(2)	24(2)	27.4(17)	-2.7(15)	8.4(16)	-6.2(18)
N3	79(3)	90(4)	78(3)	38(3)	39(3)	6(3)
C13	31(2)	40(3)	36(2)	8.1(18)	5.9(19)	8(2)
C14	31(2)	31(2)	28.7(18)	2.8(16)	3.6(16)	-0.7(18)

Table S.31. Bond Lengths for **5**.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
N1	C1	1.513(4)	C1	C2	1.515(5)
N1	C10	1.506(4)	C2	C3	1.526(5)
N1	C11	1.496(4)	C3	C4	1.515(5)
N1	C12	1.491(4)	C4	C5	1.519(5)
N2	C6	1.511(4)	C5	C6	1.510(5)
N2	C7	1.508(4)	N3	C13	1.125(5)
N2	C8	1.500(4)	C13	C14	1.441(5)
N2	C9	1.501(4)			

Table S.32. Bond Angles for **5**.

Atom	Atom	Atom	Angle/˚	Atom	Atom	Atom	Angle/˚
C10	N1	C1	110.8(3)	C9	N2	C6	111.3(2)
C11	N1	C1	106.9(3)	C9	N2	C7	108.5(3)
C11	N1	C10	108.9(3)	N1	C1	C2	115.7(3)
C12	N1	C1	111.8(3)	C1	C2	C3	109.7(3)
C12	N1	C10	109.4(3)	C4	C3	C2	113.2(3)
C12	N1	C11	109.0(3)	C3	C4	C5	113.6(3)
C7	N2	C6	107.0(3)	C6	C5	C4	110.8(3)
C8	N2	C6	112.4(2)	C5	C6	N2	115.5(3)
C8	N2	C7	108.9(3)	N3	C13	C14	179.3(5)
C8	N2	C9	108.5(3)				

Table S.33. Torsion Angles for **5**.

A	B	C	D	Angle/˚	A	B	C	D	Angle/˚
N1	C1	C2	C3	-174.2(3)	C8	N2	C6	C5	54.7(4)
C1	C2	C3	C4	-177.2(3)	C9	N2	C6	C5	-67.4(4)
C2	C3	C4	C5	179.7(3)	C10	N1	C1	C2	63.4(4)
C3	C4	C5	C6	179.8(3)	C11	N1	C1	C2	-178.1(3)
C4	C5	C6	N2	171.1(3)	C12	N1	C1	C2	-59.0(4)
C7	N2	C6	C5	174.2(3)					

Table S.34. Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for **5**.

Atom	*x*	*y*	*z*	U(eq)
H1A	7502	5640	1845	29
H1B	7217	5710	873	29
H2A	9539	5694	741	32
H2B	9882	5508	1705	32
H3A	8538	7348	1022	30
H3B	8956	7165	1978	30
H4A	10858	7392	801	32
H4B	11273	7216	1758	32
H5A	9910	9044	1080	29
H5B	10321	8867	2039	29
H6A	12287	8906	896	26
H6B	12605	8907	1868	26
H7A	13608	11405	1407	44
H7B	13873	10349	924	44
H7C	14030	10357	1903	44
H8A	10543	10641	2138	35
H8B	11585	11594	2110	35
H8C	12017	10570	2635	35
H9A	10317	10615	632	34
H9B	11642	10509	162	34
H9C	11377	11561	648	34
H10A	8223	3994	2509	44
H10B	9487	3878	1986	44
H10C	8387	2961	1978	44
H11A	5937	4241	1808	57
H11B	6129	3203	1288	57
H11C	5712	4279	830	57
H12A	9124	3983	485	43
H12B	7621	4121	38	43
H12C	8054	3046	492	43
H14A	5113	1636	10001	46
H14B	3824	1360	9367	46
H14C	3817	2389	9922	46

S.2.2. Parameters and data for X-Ray crystal structures 1, 2 and 5 refined by HAR.

Table S.35. Crystal data and structure refinement for **1**'.

Identification code	**1'**
Empirical formula	$C_{12}H_{30}Br_2N_2$
Formula weight	362.20
Temperature/K	93(2)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	5.4796(4)
b/Å	13.1109(11)
c/Å	11.5815(9)
α/°	90.000000(0)
β/°	93.580(4)
γ/°	90.000000(0)
Volume/Å^3	830.42(11)
Z	2
ρ_{calc}g/cm^3	1.449
μ/mm^{-1}	4.864
F(000)	372.0
Crystal size/mm^3	0.12 × 0.1 × 0.06
Radiation	MoKα (λ = 0.710730)
2Θ range for data collection/°	6.22 to 65.58
Index ranges	-5 ≤ h ≤ 8, -18 ≤ k ≤ 19, -17 ≤ l ≤ 13
Reflections collected	13885
Independent reflections	2351 [R_{int} = 0.0397, R_{sigma} = 0.0365]
Data/restraints/parameters	2351/0/133
Goodness-of-fit on F^2	
Final R indexes [I>=2σ (I)]	R_1 = 0.0243, wR_2 = 0.0161
Final R indexes [all data]	R_1 = 0.0243,
CCDC Number	2119853

Table S.36. Anisotropic Displacement Parameters (Å^2×10^3) for **1'**. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
N1	12.1(5)	11.1(5)	12.1(5)	0.7(4)	0.5(4)	0.0(4)
C1	16.3(7)	11.0(6)	13.7(7)	0.7(5)	-0.1(5)	-0.7(5)
C2	20.9(8)	10.6(6)	17.0(7)	-0.5(5)	-1.8(6)	0.5(5)
C4	15.7(7)	13.0(6)	17.8(7)	3.3(5)	1.9(6)	0.9(6)
C5	15.7(6)	14.4(6)	17.8(7)	-1.8(6)	0.2(5)	1.2(6)
C6	20.5(8)	15.4(7)	17.2(7)	-2.6(6)	-4.1(6)	0.8(6)
C3	22.6(8)	11.4(7)	18.7(7)	1.4(5)	1.3(6)	1.5(6)
Br1	14.65(6)	15.32(6)	13.59(6)	1.94(6)	0.82(4)	3.66(6)

Table S.37. Bond Lengths for **1'**.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
N1	C1	1.5098(16)	N1	C6	1.4914(16)
N1	C4	1.4948(16)	C1	C2	1.5150(18)
N1	C5	1.4966(17)	C2	C3	1.5234(19)

Table S.38. Bond Angles for **1'**.

Atom	Atom	Atom	Angle/˚	Atom	Atom	Atom	Angle/˚
C1	N1	C4	110.29(10)	C4	N1	C6	110.27(10)
C1	N1	C5	108.26(10)	C5	N1	C6	108.04(10)
C1	N1	C6	111.20(10)	N1	C1	C2	114.85(11)
C4	N1	C5	108.69(10)	C1	C2	C3	109.91(11)

Table S.39. Selected Bond Lengths for **1'.**

Atom	Atom	Length/Å
N1	C1	1.5098(16)
N1	C4	1.4948(16)
N1	C5	1.4966(17)
N1	C6	1.4914(16)
C1	H1A	1.034(16)
C1	H1B	1.086(16)
C1	C2	1.5150(18)
C2	H2A	1.055(17)
C2	H2B	1.075(16)
C2	C3	1.5234(19)
C4	H4A	1.083(16)
C4	H4B	1.018(17)
C4	H4C	1.057(16)
C5	H5A	1.047(17)
C5	H5B	1.054(17)
C5	H5C	1.052(17)
C6	H6A	1.051(17)
C6	H6B	1.083(17)
C6	H6C	1.016(16)
C3	H3A	1.071(18)
C3	H3B	1.084(16)

Table S.40. Selected Angles for **1'**.

Atom	Atom	Atom	Angle/˚	Atom	Atom	Atom	Angle/˚
C1	N1	C4	110.29(10)	N1	C4	H4C	106.3(9)
C1	N1	C5	108.26(10)	H4A	C4	H4B	111.3(12)

Atom	Atom	Atom	Angle/˚	Atom	Atom	Atom	Angle/˚
C1	N1	C6	111.20(10)	H4A	C4	H4C	109.9(11)
C4	N1	C5	108.69(10)	H4B	C4	H4C	113.1(12)
C4	N1	C6	110.27(10)	N1	C5	H5A	107.2(9)
C5	N1	C6	108.04(10)	N1	C5	H5B	107.6(9)
N1	C1	H1A	104.9(9)	N1	C5	H5C	107.9(9)
N1	C1	H1B	106.4(9)	H5A	C5	H5B	112.4(13)
N1	C1	C2	114.85(11)	H5A	C5	H5C	110.7(13)
H1A	C1	H1B	110.3(12)	H5B	C5	H5C	110.7(12)
C2	C1	H1A	110.9(9)	N1	C6	H6A	109.8(10)
C2	C1	H1B	109.3(9)	N1	C6	H6B	106.3(9)
C1	C2	H2A	109.6(9)	N1	C6	H6C	106.1(9)
C1	C2	H2B	111.4(9)	H6A	C6	H6B	109.0(13)
C1	C2	C3	109.91(11)	H6A	C6	H6C	112.9(12)
H2A	C2	H2B	109.1(12)	H6B	C6	H6C	112.8(13)
C3	C2	H2A	107.6(9)	C2	C3	H3A	110.6(9)
C3	C2	H2B	109.1(9)	C2	C3	H3B	107.9(9)
N1	C4	H4A	108.1(8)	H3A	C3	H3B	108.3(13)
N1	C4	H4B	107.8(9)				

Table S.41. Crystal data and structure refinement for **2'**.

Identification code	**2'**
Empirical formula	$C_{12}H_{34}Br_2N_2O_2$
Formula weight	398.23
Temperature/K	103(2)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	7.3339(13)
b/Å	18.292(3)
c/Å	7.0915(12)
α/°	90.000000(0)
β/°	108.824(4)
γ/°	90.000000(0)
Volume/Å^3	900.5(3)
Z	2
ρ_{calc}g/cm^3	1.469
μ/mm^{-1}	4.501
F(000)	412.0
Crystal size/mm^3	0.32 × 0.16 × 0.06
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.86 to 60.48
Index ranges	-10 ≤ h ≤ 10, -25 ≤ k ≤ 25, -7 ≤ l ≤ 9
Reflections collected	30772
Independent reflections	2450 [R_{int} = 0.0286, R_{sigma} = 0.0146]
Data/restraints/parameters	2450/0/133
Goodness-of-fit on F^2	
Final R indexes [I>=2σ (I)]	R_1 = 0.0173, wR_2 = 0.0216
Final R indexes [all data]	R_1 = 0.0173
CCDC Number	2119854

Table S.42. Anisotropic Displacement Parameters (Å^2×10^3) for **2'**. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	**U_{11}**	**U_{22}**	**U_{33}**	**U_{12}**	**U_{13}**	**U_{23}**
N1	12.9(5)	13.5(6)	12.1(6)	0.9(4)	5.0(5)	-1.2(4)
C1	14.9(6)	12.9(7)	13.9(8)	1.6(5)	6.2(6)	0.5(6)
C2	15.1(6)	13.6(7)	14.0(8)	2.5(5)	6.5(6)	0.7(6)
C3	14.4(6)	14.1(7)	13.5(8)	0.1(5)	5.6(6)	0.1(6)
C4	24.5(7)	15.9(7)	24.6(10)	5.6(6)	12.7(7)	-0.5(7)
C5	17.1(7)	32.8(9)	12.8(8)	1.2(6)	4.6(6)	-0.6(7)
C6	16.1(6)	15.6(7)	22.7(9)	-1.9(5)	8.9(6)	-2.1(6)
Br1	14.73(7)	14.06(8)	15.65(9)	0.53(5)	5.68(6)	-0.86(5)
O1	29.6	34.8	47.3	-2.5	12.6	-11.4

Table S.43. Bond Lengths for **2'**.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
N1	C1	1.5119(17)	N1	C6	1.4986(16)
N1	C4	1.4964(16)	C1	C2	1.5249(18)
N1	C5	1.4962(18)	C2	C3	1.5270(19)

Table S.44. Bond Angles for **2'**.

Atom	Atom	Atom	Angle/˚	Atom	Atom	Atom	Angle/˚
C1	N1	C4	107.83(10)	C4	N1	C6	108.13(11)
C1	N1	C5	111.18(11)	C5	N1	C6	109.46(11)
C1	N1	C6	111.14(10)	N1	C1	C2	114.65(11)
C4	N1	C5	109.02(11)	C1	C2	C3	110.36(11)

Table S.45. Selected Bond Lengths for **2'**.

Atom	Atom	Length/Å
N1	C1	1.5119(17)
N1	C4	1.4964(16)
N1	C5	1.4962(18)
N1	C6	1.4986(16)
C1	H1A	1.101(15)
C1	H1B	1.083(17)
C1	C2	1.5249(18)
C2	H2A	1.096(15)
C2	H2B	1.116(16)
C2	C3	1.5270(19)
C3	H3A	1.025(14)
C3	H3B	1.042(14)
C4	H4A	1.076(17)
C4	H4B	1.070(15)
C4	H4C	1.011(19)
C5	H5A	1.07(2)
C5	H5B	1.069(19)
C5	H5C	1.112(19)
C6	H6A	1.168(18)
C6	H6B	1.035(16)
C6	H6C	1.128(17)
O1	H1O	1.010442(0)
O1	H2O	1.121890(0)

Table S.46. Selected Angles for **2'**.

Atom	Atom	Atom	Angle/˚	Atom	Atom	Atom	Angle/˚
C1	N1	C4	107.83(10)	H3A	C3	H3B	110.5(11)
C1	N1	C5	111.18(11)	N1	C4	H4A	108.9(9)
C1	N1	C6	111.14(10)	N1	C4	H4B	108.8(8)
C4	N1	C5	109.02(11)	N1	C4	H4C	110.1(9)
C4	N1	C6	108.13(11)	H4A	C4	H4B	112.0(11)
C5	N1	C6	109.46(11)	H4A	C4	H4C	113.5(13)
N1	C1	H1A	106.6(8)	H4B	C4	H4C	103.4(12)
N1	C1	H1B	104.1(9)	N1	C5	H5A	106.7(10)
N1	C1	C2	114.65(11)	N1	C5	H5B	109.0(11)
H1A	C1	H1B	106.0(10)	N1	C5	H5C	110.9(9)
C2	C1	H1A	112.4(8)	H5A	C5	H5B	110.1(14)
C2	C1	H1B	112.4(8)	H5A	C5	H5C	111.7(13)
C1	C2	H2A	113.6(8)	H5B	C5	H5C	108.4(14)
C1	C2	H2B	112.0(8)	N1	C6	H6A	107.6(8)
C1	C2	C3	110.36(11)	N1	C6	H6B	108.7(9)
H2A	C2	H2B	103.6(11)	N1	C6	H6C	109.2(8)
C3	C2	H2A	106.4(8)	H6A	C6	H6B	111.1(13)
C3	C2	H2B	110.5(8)	H6A	C6	H6C	106.5(12)
C2	C3	H3A	108.4(9)	H6B	C6	H6C	113.5(13)
C2	C3	H3B	111.6(8)	H1O	O1	H2O	97.3(0)

Table S.47. Crystal data and structure refinement for **5'**.

Identification code	**5'**
Empirical formula	$C_{14}H_{33}I_2N_3$
Formula weight	497.2472
Temperature/K	103(2)
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	9.920(2)
b/Å	12.776(2)
c/Å	16.440(3)
α/°	90.000000(0)
β/°	96.07(2)
γ/°	90.000000(0)
Volume/Å^3	2071.9(7)
Z	4
ρ_{calc}g/cm^3	1.594
μ/mm^{-1}	3.031
F(000)	976.0
Crystal size/mm^3	0.14 × 0.08 × 0.04
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.04 to 61.02
Index ranges	-13 ≤ h ≤ 14, -17 ≤ k ≤ 18, -23 ≤ l ≤ 23
Reflections collected	21599
Independent reflections	4547 [R_{int} = 0.0489, R_{sigma} = 0.0631]
Data/restraints/parameters	4547/0/304
Goodness-of-fit on F^2	
Final R indexes [I>=2σ (I)]	R_1 = 0.0404, wR_2 = 0.0235
Final R indexes [all data]	R_1 = 0.0404
CCDC Number	2119855

Table S.48. Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for **5'**. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
I1	19.64(13)	19.40(13)	26.92(12)	-1.22(11)	3.27(10)	0.86(10)
I2	24.01(14)	20.73(14)	26.17(12)	-1.49(12)	2.52(10)	-2.83(11)
N1	29.9(19)	17.7(17)	24.7(15)	-7.2(14)	5.4(14)	-2.4(13)
N2	18.8(17)	18.2(16)	20.4(14)	-4.9(14)	-0.5(12)	0.4(13)
C1	28(2)	16(2)	30(2)	-6.4(17)	7.6(18)	-1.4(16)
C2	30(2)	18(2)	35(2)	-6.4(19)	2.9(19)	-2.2(18)
C3	29(2)	15(2)	37(2)	-4.6(18)	4(2)	0.6(18)
C4	26(2)	15(2)	43(2)	-3.1(19)	0(2)	-1.6(18)
C5	24(2)	19(2)	34(2)	-1.2(18)	7.2(18)	-1.3(17)
C6	25(2)	19.0(19)	24.7(19)	-1.8(18)	2.9(17)	-1.1(17)
C7	17(2)	30(3)	42(2)	-5.0(19)	1.3(19)	-3(2)
C8	32(2)	20(2)	22.1(18)	-2(2)	3.1(17)	-0.3(17)
C9	24(2)	23(2)	22.3(18)	-3(2)	-0.2(17)	-1.5(16)
C10	51(3)	20(2)	24(2)	-6(2)	5(2)	-0.1(18)
C11	29(3)	30(3)	64(3)	-9(2)	16(2)	-8(3)
C12	37(3)	24(2)	29(2)	-5(2)	8(2)	-2.1(18)
N3	82(3)	97(4)	78(3)	5(3)	41(3)	41(3)
C13	37(3)	41(3)	36(2)	5(2)	11(2)	14(2)
C14	33(3)	34(3)	30(2)	-2(2)	4(2)	3.1(19)

Table S.49. Bond Lengths for **5'**.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
N1	C1	1.514(4)	C1	C2	1.517(5)
N1	C10	1.506(5)	C2	C3	1.527(5)
N1	C11	1.501(5)	C3	C4	1.522(5)
N1	C12	1.491(4)	C4	C5	1.522(5)
N2	C6	1.509(4)	C5	C6	1.512(5)
N2	C7	1.501(5)	N3	C13	1.131(5)
N2	C8	1.496(4)	C13	C14	1.432(5)
N2	C9	1.499(4)			

Table S.50. Bond Angles for **5'**.

Atom	Atom	Atom	Angle/˚	Atom	Atom	Atom	Angle/˚
C1	N1	C10	111.0(3)	C7	N2	C9	108.6(3)
C1	N1	C11	106.8(3)	C8	N2	C9	108.9(3)
C1	N1	C12	111.8(3)	N1	C1	C2	115.3(3)
C10	N1	C11	109.2(3)	C1	C2	C3	109.2(3)
C10	N1	C12	109.6(3)	C2	C3	C4	112.8(3)
C11	N1	C12	108.3(3)	C3	C4	C5	113.5(3)
C6	N2	C7	107.0(3)	C4	C5	C6	110.6(3)
C6	N2	C8	112.6(3)	N2	C6	C5	115.4(3)
C6	N2	C9	111.2(3)	N3	C13	C14	179.4(5)
C7	N2	C8	108.5(3)				

Table S.51. Selected Bond Lengths for **5'**.

Atom	Atom	Length/Å
N1	C1	1.514(4)
N1	C10	1.506(5)
N1	C11	1.501(5)
N1	C12	1.491(4)
N2	C6	1.509(4)
N2	C7	1.501(5)
N2	C8	1.496(4)
N2	C9	1.499(4)
C1	H1A	1.11(4)
C1	H1B	1.10(4)
C1	C2	1.517(5)
C2	H2A	1.07(4)
C2	H2B	1.08(4)
C2	C3	1.527(5)
C3	H3A	1.01(4)
C3	H3B	1.14(5)
C3	C4	1.522(5)
C4	H4A	1.16(5)
C4	H4B	0.98(4)
C4	C5	1.522(5)
C5	H5A	1.11(4)
C5	H5B	1.09(4)
C5	C6	1.512(5)
C6	H6A	1.10(4)
C6	H6B	1.05(3)
C7	H7A	1.08(5)
C7	H7B	1.13(4)
C7	H7C	1.15(4)
C8	H8A	1.03(3)

Atom	Atom	Length/Å
C8	H8B	1.11(4)
C8	H8C	1.09(4)
C9	H9A	1.12(4)
C9	H9B	1.07(3)
C9	H9C	1.10(4)
C10	H10A	1.11(4)
C10	H10B	1.07(4)
C10	H10C	1.10(5)
C11	H11A	0.99(5)
C11	H11B	1.19(4)
C11	H11C	1.09(4)
C12	H12A	1.07(4)
C12	H12B	1.08(4)
C12	H12C	1.13(3)
N3	C13	1.131(5)
C13	C14	1.432(5)
C14	H14A	1.07(4)
C14	H14B	1.07(5)
C14	H14C	1.14(5)

Table S.52. Selected Angles for **5'**.

Atom	Atom	Atom	Angle/˚	Atom	Atom	Atom	Angle/˚
C1	N1	C10	111.0(3)	C5	C6	H6B	109.8(19)
C1	N1	C11	106.8(3)	H6A	C6	H6B	113(3)
C1	N1	C12	111.8(3)	N2	C7	H7A	110(2)
C10	N1	C11	109.2(3)	N2	C7	H7B	107(2)
C10	N1	C12	109.6(3)	N2	C7	H7C	107(2)
C11	N1	C12	108.3(3)	H7A	C7	H7B	116(3)
C6	N2	C7	107.0(3)	H7A	C7	H7C	104(3)
C6	N2	C8	112.6(3)	H7B	C7	H7C	112(3)
C6	N2	C9	111.2(3)	N2	C8	H8A	107(2)
C7	N2	C8	108.5(3)	N2	C8	H8B	108.5(18)
C7	N2	C9	108.6(3)	N2	C8	H8C	109(2)
C8	N2	C9	108.9(3)	H8A	C8	H8B	118(3)
N1	C1	H1A	105(2)	H8A	C8	H8C	108(3)
N1	C1	H1B	104.5(19)	H8B	C8	H8C	106(3)
N1	C1	C2	115.3(3)	N2	C9	H9A	106.4(19)
H1A	C1	H1B	111(3)	N2	C9	H9B	109.4(18)
C2	C1	H1A	111(2)	N2	C9	H9C	106.5(17)
C2	C1	H1B	111(2)	H9A	C9	H9B	114(3)
C1	C2	H2A	107(2)	H9A	C9	H9C	111(3)
C1	C2	H2B	113(2)	H9B	C9	H9C	109(3)
C1	C2	C3	109.2(3)	N1	C10	H10A	107(2)
H2A	C2	H2B	109(3)	N1	C10	H10B	104.1(19)

Atom	Atom	Atom	Angle/˚	Atom	Atom	Atom	Angle/˚
C3	C2	H2A	112(3)	N1	C10	H10C	110(2)
C3	C2	H2B	108(2)	H10A	C10	H10B	117(3)
C2	C3	H3A	115(3)	H10A	C10	H10C	105(3)
C2	C3	H3B	113(3)	H10B	C10	H10C	114(3)
C2	C3	C4	112.8(3)	N1	C11	H11A	103(3)
H3A	C3	H3B	113(3)	N1	C11	H11B	107(2)
C4	C3	H3A	99(3)	N1	C11	H11C	106(2)
C4	C3	H3B	102(3)	H11A	C11	H11B	115(4)
C3	C4	H4A	108(2)	H11A	C11	H11C	111(3)
C3	C4	H4B	106(3)	H11B	C11	H11C	114(3)
C3	C4	C5	113.5(3)	N1	C12	H12A	108(2)
H4A	C4	H4B	108(3)	N1	C12	H12B	109(2)
C5	C4	H4A	106(2)	N1	C12	H12C	109.7(19)
C5	C4	H4B	115(3)	H12A	C12	H12B	103(3)
C4	C5	H5A	112(2)	H12A	C12	H12C	114(3)
C4	C5	H5B	108(2)	H12B	C12	H12C	112(3)
C4	C5	C6	110.6(3)	N3	C13	C14	179.4(5)
H5A	C5	H5B	105(3)	C13	C14	H14A	108(2)
C6	C5	H5A	112(2)	C13	C14	H14B	109(3)
C6	C5	H5B	109(2)	C13	C14	H14C	109(2)
N2	C6	C5	115.4(3)	H14A	C14	H14B	112(3)
N2	C6	H6A	104(2)	H14A	C14	H14C	110(3)
N2	C6	H6B	104.5(18)	H14B	C14	H14C	109(3)
C5	C6	H6A	110(2)				

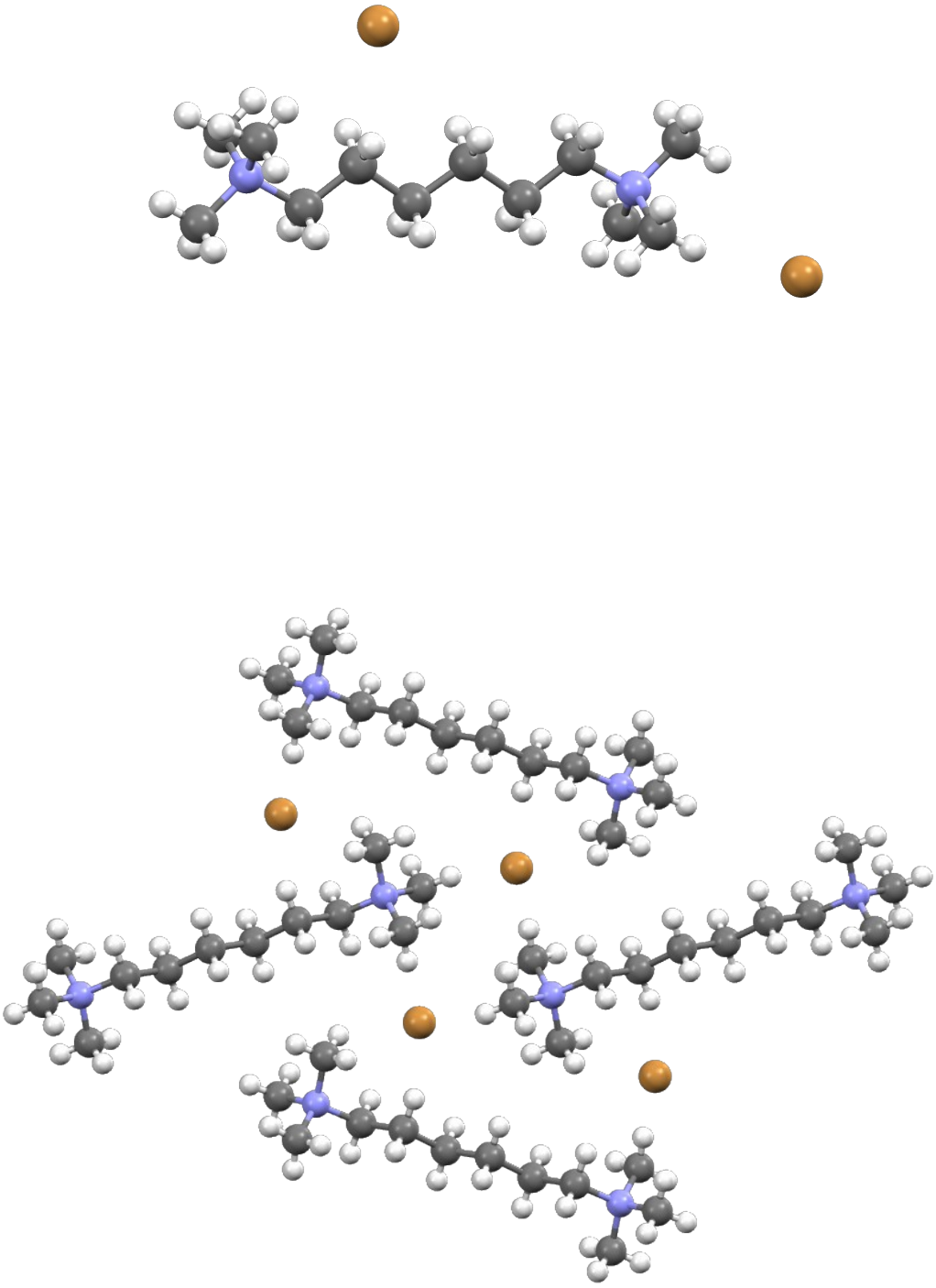

Figure S.1. Asymmetric unit (above) and crystal packing (below) of crystal structure **1**.

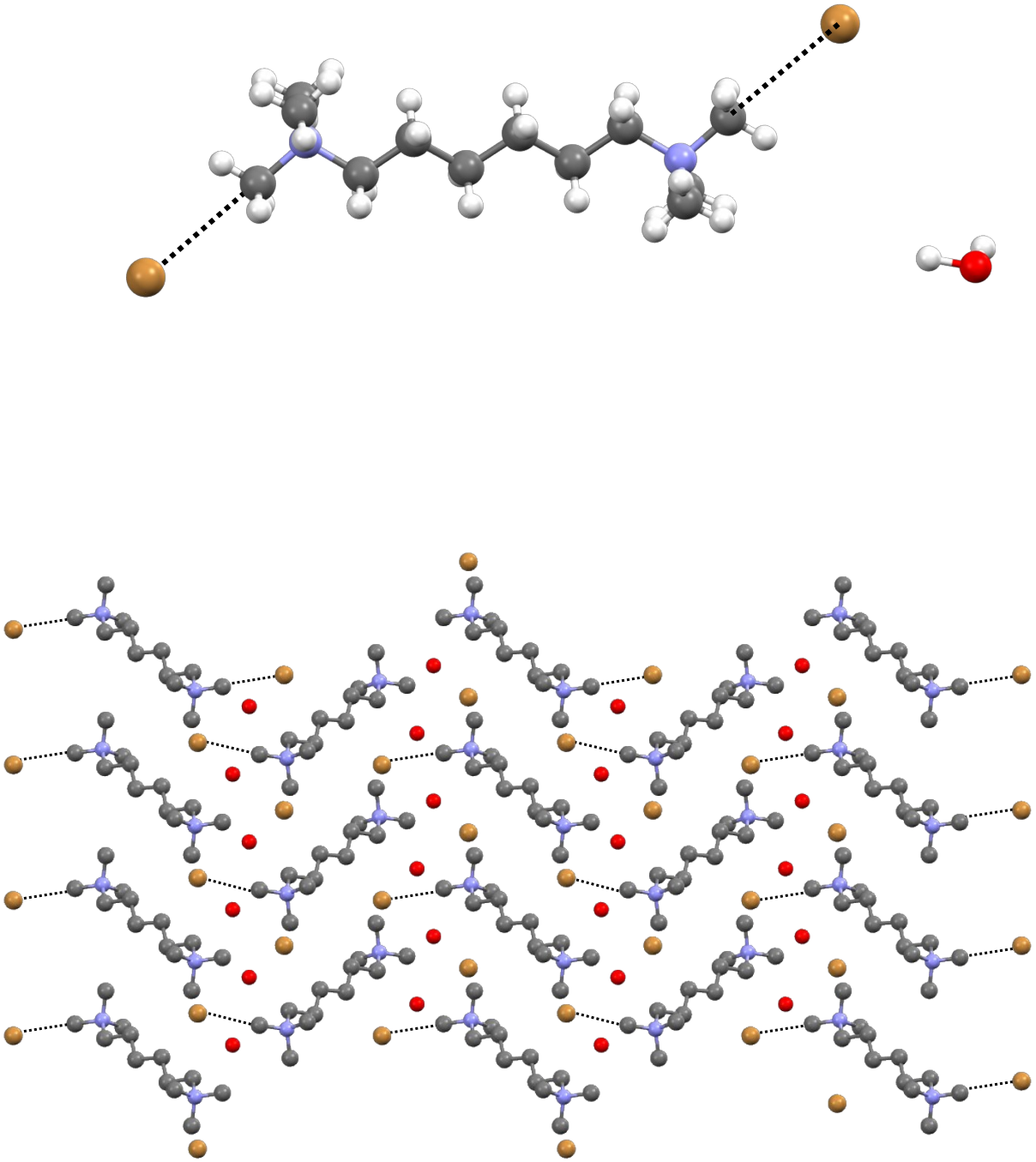

Figure S.2. Asymmetric unit (above) and crystal packing (below) of crystal structure **2**. Tetrel bonds are black dotted lines. Hydrogens removed for clarity.

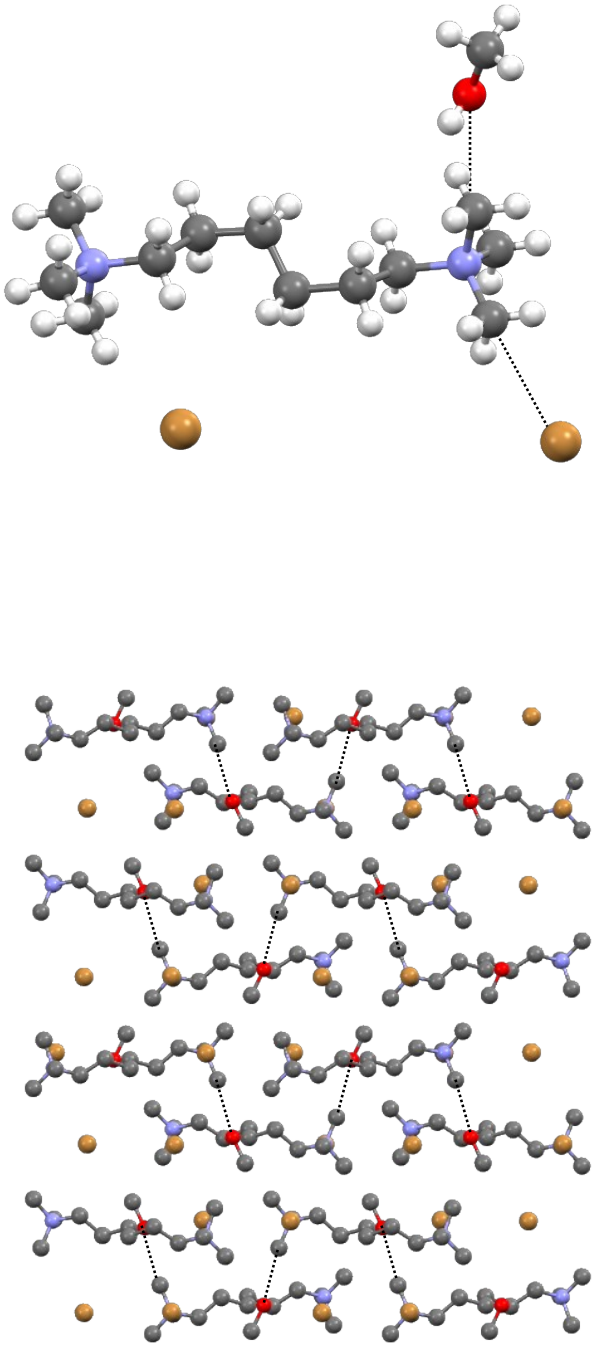

Figure S.3. Asymmetric unit (above) and crystal packing (below) of crystal structure **3**. Tetrel bonds are black dotted lines. Hydrogens removed for clarity.

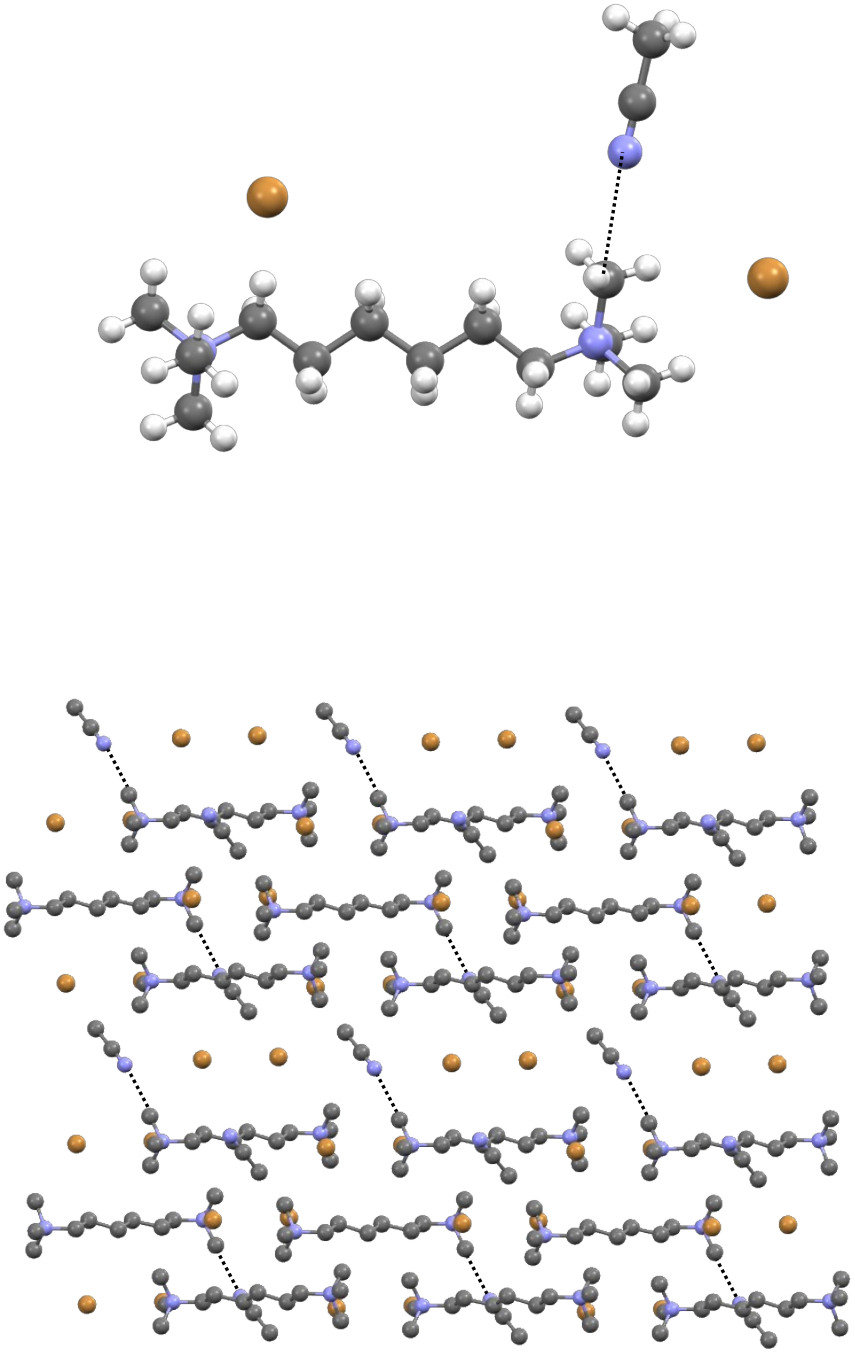

Figure S.4. Asymmetric unit (above) and crystal packing (below) of crystal structure **4**. Tetrel bonds are black dotted lines. Hydrogens removed for clarity.

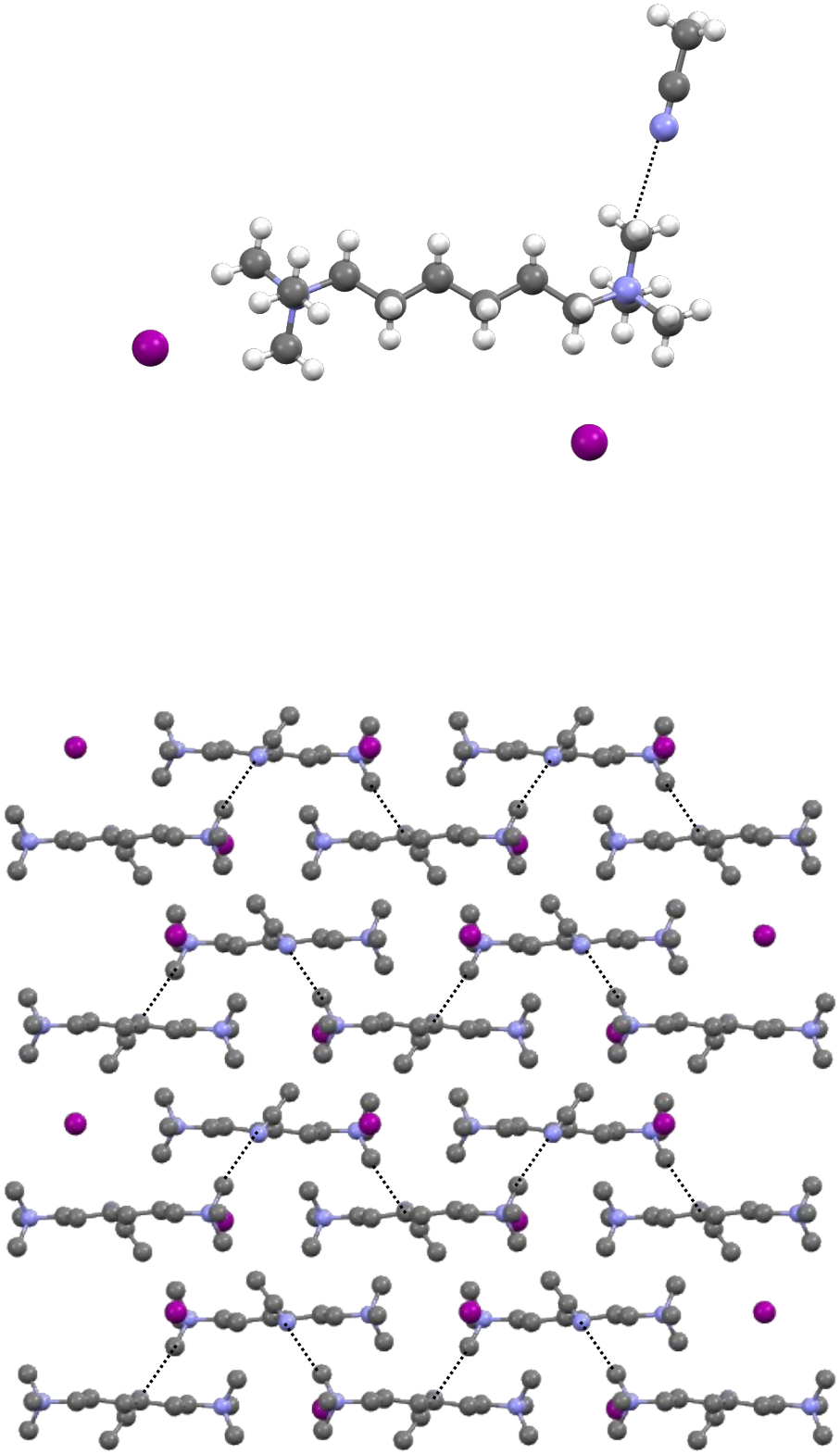

Figure S.5. Asymmetric unit (above) and crystal packing (below) of crystal structure **5**. Tetrel bonds are black dotted lines. Hydrogens removed for clarity.

S.3. CSD Surveys.

Table S.53. Hexamethonium (1,6-bis-(trimethyl ammonium) hexane) structures present on the CSD. In bold structures that present a short contact between one of the methyl's carbons and an electron rich atom (atoms considered N, P, O, S, Se, F, Cl, Br, I) establishing a N^+-C···Nu angle comprised between 160 and 180°. In bold and red entries where the contact is shorter than the sum of their respective vdW radii, in bold and black contacts where the contact is shorter than the sum plus 0.2 Å.

DIQBIQ	**HMENAM01**	**NUTTAY**	**URUBUF**
DIQBOW	HMTMAC	NUTTAY01	**XEPDEB**
DIQBUC	HMTMAC01	**SOFYER**	**YEPGOQ**
FUGGET	MUXSUT	**TIBROL**	**PUPBEK**
HMACQM	**NUTSOL**	URUBIT	VUGNUJ
HMENAM	NUTSUR	URUBOZ	VUGNUJ01

Table S.54. Octamethonium (1,8-bis-(trimethyl ammonium) octane) structures present on the CSD. In bold structures that present a short contact between one of the methyl's carbons and an electron rich atom (atoms considered N, P, O, S, Se, F, Cl, Br, I) establishing a N^+-C···Nu angle comprised between 160 and 180°. In bold and red entries where the contact is shorter than the sum of their respective vdW radii, in bold and black contacts where the contact is shorter than the sum plus 0.2 Å.

XOTZOW	XOTZUC	ZIHXOG	

Table S.55. Decamethonium (1,10-bis(trimethylammonium) decane) structures present on the CSD. In bold structures that present a short contact between one of the methyl's carbons and an electron rich atom (atoms considered N, P, O, S, Se, F, Cl, Br, I) establishing a N^+-C···Nu angle comprised between 160 and 180°. In bold and red entries where the contact is shorter than the sum of their respective vdW radii, in bold and black contacts where the contact is shorter than the sum plus 0.2 Å.

DIMENAM	SIHYOZ	**XOVBAM**	
SIHFAQ	**SIHYUF**	**XOVBEQ**	
SIHYIT	**WESLAK**	XOVBIU	

S.4. Fundamentals of Hirshfeld Atom Refinement

The Hirshfeld atom refinement (HAR)[3,4,5] is a self-consistent refinement procedure based on the following steps.

1. Quantum chemical calculation on a system that at least corresponds to the asymmetric unit of the target crystal structure. The starting geometry is usually the one that is obtained from the preliminary IAM refinement.
2. Subdivision of the obtained electron density $\rho_0(r)$ (associated with the quantum chemical calculation at point 1) into atomic contributions using the Hirshfeld stockholder partitioning technique[6,7]. According to this method, the atomic density distribution for each atom is given by

$$\rho_A(r) = w_A(r)\,\rho_0(r) \quad (S1),$$

where $w_A(r)$ is the Hirshfeld weight function provided by the ration between the spherically averaged atomic density of the atom under consideration (ρ_A^o) and the promolecular density, which is the sum of the spherically averaged atomic densities of all the atoms forming the investigated system:

$$w_A(r) = \frac{\rho_A^o(r)}{\sum_{B=1}^{Natoms} \rho_B^o(r)} \quad (S2)$$

3. Calculation of the atomic form factors through Fourier transformation of the atomic densities obtained at point 2.
4. Calculation of the global structure factors $\{F_h^{calc}\}$ as sum of the atomic form factors resulting from point 3.
5. Least-squares minimization of the χ^2 statistical agreement between experimental and calculated structure factor amplitudes with respect to the scale factor η (see equation (S3) below), atomic coordinates and ADPs. The χ^2 statistical agreement is given by the following relation:

$$\chi^2 = \frac{1}{N_r - N_p}\sum_h \frac{\left(\eta\left|F_h^{calc}\right| - \left|F_h^{exp}\right|\right)^2}{\sigma_h^2} \qquad (S3)$$

with N_r as the number of reflections, N_p as the number of parameters in the model, $\left|F_h^{calc}\right|$ and $\left|F_h^{exp}\right|$ as the calculated and experimental structure factor amplitudes, respectively, for the reflection corresponding to the Miller indices triplet $h = (h,k,l)$, σ_h as the experimental error associated with the experimental structure factor amplitude $\left|F_h^{exp}\right|$, and η as an overall (h-independent) factor that puts $\left|F_h^{calc}\right|$ on the same scale of $\left|F_h^{exp}\right|$.

6. Check of convergence on the atomic structural parameters (i.e., atomic coordinates and ADPs). When convergence is achieved, the iterative procedure ends, and electronic properties of the system may be calculated exploiting the wave function / electron density corresponding to the converged structure. Otherwise, the new geometry is exploited to start a new iteration and, particularly, to carry out a new quantum chemical calculation (see point 1).

As already mentioned in the main text, it is worth noting that, in order to properly account for the crystal field effects, the quantum mechanical computations at point 1 can be also performed by embedding the reference system through a cluster of point charges and dipoles. They are generally placed on all those atoms of the surrounding moieties of the crystal that have at least one atom at a distance lower than 8 Å from the reference system considered for the quantum chemical calculations.

S.5 References

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