

Supporting Information

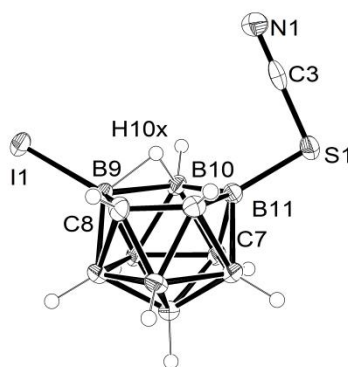


Figure 1. Molecular structure of the anion in compound **9**. NMe₄ cation is omitted for clarity. Thermal ellipsoids are drawn at the 50 % level of probability. Selected bond lengths (pm) and bond angles (deg): C7–C8 154.6(6), C7–B11 158.1(5), C8–B9 160.7(6), B9–B10 186.0(5), B10–B11 182.7(6), I1–B9 219.8(4), S1–B11 189.6(4), H10x–B9–B10 39.62(8), H10x–B10–B9 49.60(9). Crystallographic data: C₇H₂₂B₉IN₂S, *M_r* = 390.52, orthorhombic, *a* = 692.82(2) pm, *b* = 1051.39(2) pm, *c* = 2418.00(4) pm, α = 90°, β = 90°, γ = 90°, *V* = 1761.33(7) Å³, *P*₂₁₂₁₂₁, *Z* = 4, observed reflections (*I* > 2σ(*I*)): 11805, unique reflections: 3591, *R*_{int} = 0.0288, *R*₁ (on *F* for observed reflections) = 0.0281, *wR*₂ (on *F*² for observed reflections) = 0.0562. The crystal was a racemic twin and was solved in two domains with both enantiomers present.

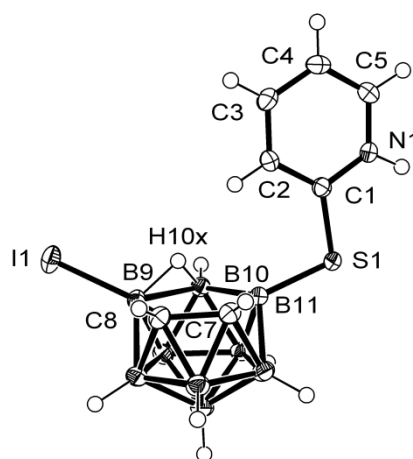


Figure 2. Molecular structure of compound **10**. The thermal ellipsoids are drawn at the 50 % level of probability. Selected bond lengths (pm) and bond angles (deg): C7–C8 154.7(3), C7–B11 160.6(3), C8–B9 161.7(3), B9–B10 185.4(3), B10–B11 180.0(3), I1–B9 218.3(2), S1–B11 187.4(2), H10x–B9–B10 38.09(8), H10x–B10–B9 45.33(9). Crystallographic data: C₇H₁₅B₉INS, *M_r* = 369.45, monoclinic, *a* = 704.08(1) pm, *b* = 1508.71(2) pm, *c* = 1420.86(2) pm, α = 90°, β = 99.017(2)°, γ = 90°, *V* =

1490.66(4) Å³, $P2_1/n$, $Z = 4$, observed reflections ($I > 2\sigma(I)$): 9585, unique reflections: 3046, $R_{int} = 0.0208$, $R1$ (on F for observed reflections) = 0.0186, $wR2$ (on F^2 for observed reflections) = 0.0454.