Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.


## Contents

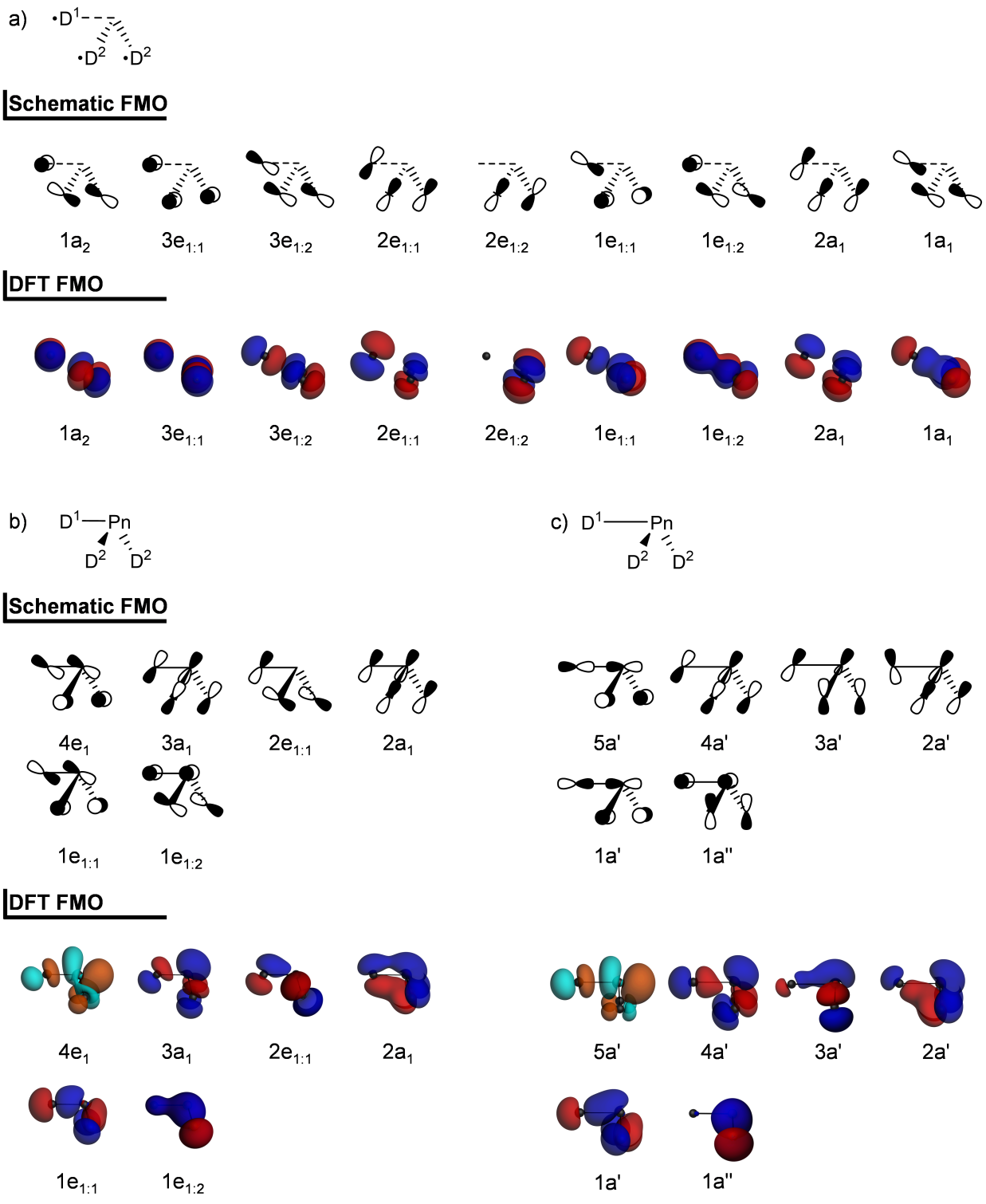


**Fig. S1.** Schematic FMO and DFT MO isosurfaces (at 0.04 a.u.) for (a) the $(D^{\bullet})_3$ molecule in its quadruplet valence state at $C_{3v}$ symmetry and for the $D_3Pn$ fragment in (b) the ground state at $C_{2v}$ symmetry and in (c) the geometry of the complex at $C_s$ symmetry.

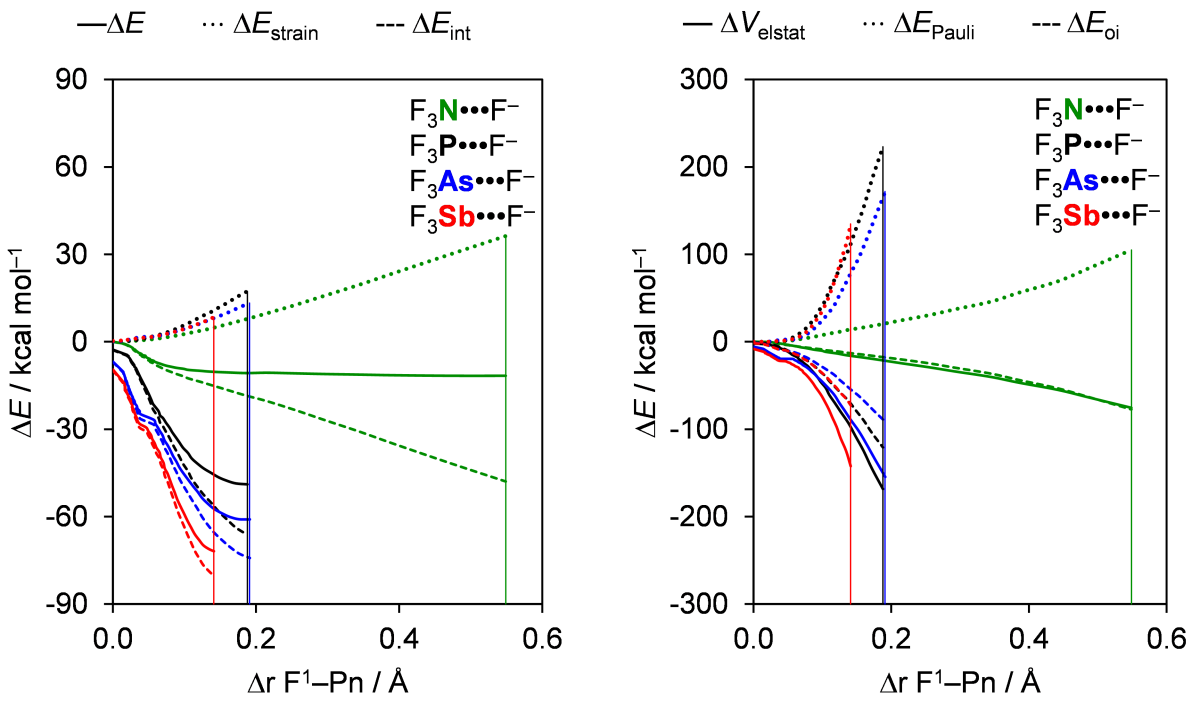


**Fig. S2.** Activation strain (left panel) and energy decomposition (right panel) analyses of $F_3Pn{\bullet\bullet\bullet}F^-$ pnictogen-bonded complexes (green, Pn = N; black, Pn = P; blue, Pn = As; red, Pn = Sb). The vertical lines indicate the position of the stationary points.

**Table S1.** Activation strain analyses (in kcal mol$^{-1}$) of $D_3Pn\bullet\bullet\bullet A^-$ pnictogen bonds at the equilibrium geometries (in Å, deg.).[a]

| $D_3Pn\cdots A^-$ | $\Delta E$ | $\Delta E_{strain}$ | $\Delta E_{int}$ | $r_{Pn\cdots A^-}$ | $r_{Pn-D^1}$ | $r_{Pn-D^2}$ | $\Delta r_{Pn-D^1}$ | $\Delta r_{Pn-D^2}$ | $\Theta_1$ | $\Theta_2$ | $\Theta_3$ | $\Delta\Theta_1$ | $\Delta\Theta_2$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $F_3N\cdots F^-$ | –11.8 | 32.5 | –44.3 | 1.859 | 1.859 | 1.339 | 0.503 | –0.017 | 93.0 | 102.4 | 170.3 | –8.9 | 0.5 |
| $F_3N\cdots Cl^-$ | –3.5 | 0.8 | –4.3 | 3.239 | 1.404 | 1.347 | 0.048 | –0.009 | 100.4 | 102.3 | 168.3 | –1.5 | 0.4 |
| $F_3N\cdots Br^-$ | –2.9 | 0.5 | –3.5 | 3.484 | 1.396 | 1.348 | 0.040 | –0.008 | 100.7 | 102.2 | 166.8 | –1.2 | 0.3 |
| $Cl_3N\cdots F^-$ | –30.4 | 55.7 | –86.1 | 1.416 | 3.243 | 1.754 | 1.490 | 0.001 | 82.0 | 108.1 | 170.7 | –25.7 | 0.4 |
| $Cl_3N\cdots Cl^-$ | –5.6 | 22.9 | –28.5 | 2.328 | 2.328 | 1.757 | 0.575 | 0.004 | 99.9 | 106.9 | 146.6 | –7.8 | –0.8 |
| $Cl_3N\cdots Br^-$ | –6.2 | 3.5 | –9.7 | 2.920 | 1.902 | 1.777 | 0.149 | 0.024 | 104.9 | 106.8 | 145.6 | –2.8 | –0.9 |
| $Br_3N\cdots F^-$ | –30.2 | 53.2 | –83.3 | 1.411 | 3.323 | 1.928 | 1.417 | 0.022 | 84.5 | 108.5 | 165.7 | –24.0 | 0.0 |
| $Br_3N\cdots Cl^-$ | –8.0 | 2.0 | –10.0 | 2.813 | 2.017 | 1.932 | 0.111 | 0.026 | 105.7 | 107.7 | 149.4 | –2.8 | –0.8 |
| $Br_3N\cdots Br^-$ | –7.0 | 17.2 | –24.2 | 2.322 | 2.322 | 1.972 | 0.416 | 0.066 | 105.4 | 106.8 | 127.2 | –3.1 | –1.7 |
| $F_3P\cdots F^-$ | –48.9 | 17.4 | –66.4 | 1.753 | 1.753 | 1.608 | 0.189 | 0.044 | 86.9 | 98.7 | 189.4 | –10.6 | 1.2 |
| $F_3P\cdots Cl^-$ | –16.0 | 4.4 | –20.4 | 2.700 | 1.647 | 1.580 | 0.083 | 0.016 | 91.9 | 97.8 | 183.4 | –5.6 | 0.3 |
| $F_3P\cdots Br^-$ | –12.9 | 3.0 | –15.9 | 2.982 | 1.631 | 1.576 | 0.067 | 0.012 | 92.9 | 97.7 | 181.6 | –4.6 | 0.2 |
| $Cl_3P\cdots F^-$ | –67.4 | 31.8 | –99.3 | 1.649 | 2.627 | 2.103 | 0.572 | 0.048 | 88.6 | 100.2 | 181.4 | –11.8 | –0.2 |
| $Cl_3P\cdots Cl^-$ | –25.5 | 14.4 | –39.8 | 2.370 | 2.370 | 2.089 | 0.315 | 0.034 | 91.7 | 100.1 | 174.6 | –8.7 | –0.3 |
| $Cl_3P\cdots Br^-$ | –20.5 | 10.7 | –31.3 | 2.617 | 2.318 | 2.085 | 0.263 | 0.030 | 92.8 | 100.1 | 172.9 | –7.6 | –0.3 |
| $Br_3P\cdots F^-$ | –71.0 | 30.2 | –101.2 | 1.637 | 2.874 | 2.272 | 0.647 | 0.045 | 89.6 | 100.3 | 175.4 | –11.3 | –0.6 |
| $Br_3P\cdots Cl^-$ | –28.5 | 15.4 | –43.9 | 2.312 | 2.609 | 2.265 | 0.382 | 0.038 | 92.0 | 100.2 | 172.0 | –8.9 | –0.7 |
| $Br_3P\cdots Br^-$ | –23.4 | 11.9 | –35.3 | 2.550 | 2.550 | 2.261 | 0.323 | 0.034 | 93.0 | 100.2 | 170.6 | –7.9 | –0.7 |
| $F_3As\cdots F^-$ | –61.0 | 12.6 | –73.6 | 1.900 | 1.900 | 1.757 | 0.183 | 0.040 | 87.1 | 97.2 | 188.7 | –8.7 | 1.4 |
| $F_3As\cdots Cl^-$ | –28.7 | 6.1 | –34.9 | 2.595 | 1.836 | 1.744 | 0.119 | 0.027 | 89.5 | 95.8 | 182.3 | –6.3 | 0.0 |
| $F_3As\cdots Br^-$ | –24.2 | 4.8 | –29.0 | 2.820 | 1.820 | 1.741 | 0.103 | 0.024 | 90.2 | 95.6 | 180.4 | –5.6 | –0.2 |
| $Cl_3As\cdots F^-$ | –70.0 | 18.7 | –88.7 | 1.850 | 2.585 | 2.229 | 0.406 | 0.050 | 91.6 | 98.7 | 175.7 | –7.5 | –0.4 |
| $Cl_3As\cdots Cl^-$ | –35.1 | 11.3 | –46.4 | 2.465 | 2.465 | 2.223 | 0.286 | 0.044 | 93.4 | 98.2 | 169.7 | –5.7 | –0.9 |
| $Cl_3As\cdots Br^-$ | –30.1 | 9.6 | –39.7 | 2.668 | 2.437 | 2.220 | 0.258 | 0.041 | 93.9 | 98.2 | 167.9 | –5.2 | –0.9 |
| $Br_3As\cdots F^-$ | –71.5 | 17.3 | –88.8 | 1.843 | 2.789 | 2.391 | 0.447 | 0.049 | 93.0 | 99.1 | 172.0 | –6.7 | –0.6 |
| $Br_3As\cdots Cl^-$ | –37.0 | 10.7 | –47.6 | 2.438 | 2.663 | 2.389 | 0.321 | 0.047 | 94.7 | 98.6 | 165.7 | –5.0 | –1.1 |
| $Br_3As\cdots Br^-$ | –32.0 | 9.2 | –41.2 | 2.634 | 2.634 | 2.387 | 0.292 | 0.045 | 95.2 | 98.6 | 164.0 | –4.5 | –1.1 |
| $F_3Sb\cdots F^-$ | –72.0 | 8.8 | –80.8 | 2.037 | 2.037 | 1.930 | 0.144 | 0.037 | 85.4 | 97.0 | 193.9 | –8.9 | 2.7 |
| $F_3Sb\cdots Cl^-$ | –38.9 | 5.8 | –44.7 | 2.643 | 2.005 | 1.923 | 0.112 | 0.030 | 87.0 | 95.1 | 188.3 | –7.3 | 0.8 |
| $F_3Sb\cdots Br^-$ | –33.6 | 5.0 | –38.7 | 2.840 | 1.996 | 1.921 | 0.103 | 0.028 | 87.5 | 94.8 | 186.7 | –6.8 | 0.5 |
| $Cl_3Sb\cdots F^-$ | –77.1 | 12.3 | –89.4 | 2.017 | 2.649 | 2.399 | 0.301 | 0.051 | 89.4 | 97.6 | 183.7 | –7.6 | 0.6 |
| $Cl_3Sb\cdots Cl^-$ | –42.7 | 8.9 | –51.7 | 2.592 | 2.592 | 2.393 | 0.244 | 0.045 | 90.5 | 96.7 | 178.4 | –6.5 | –0.3 |
| $Cl_3Sb\cdots Br^-$ | –37.3 | 8.0 | –45.3 | 2.780 | 2.577 | 2.391 | 0.229 | 0.043 | 90.9 | 96.6 | 177.0 | –6.1 | –0.4 |
| $Br_3Sb\cdots F^-$ | –77.7 | 11.5 | –89.2 | 2.014 | 2.842 | 2.559 | 0.332 | 0.049 | 90.5 | 98.0 | 181.2 | –7.2 | 0.3 |
| $Br_3Sb\cdots Cl^-$ | –43.5 | 8.5 | –52.0 | 2.580 | 2.782 | 2.556 | 0.272 | 0.046 | 91.6 | 97.2 | 175.6 | –6.1 | –0.5 |
| $Br_3Sb\cdots Br^-$ | –38.1 | 7.7 | –45.8 | 2.766 | 2.766 | 2.555 | 0.256 | 0.045 | 91.9 | 97.0 | 174.2 | –5.8 | –0.7 |

[a] Computed at ZORA-M06/QZ4P.

**Table S2.** Energy decomposition analyses (in kcal mol$^{-1}$) of $D_3Pn\cdots A^-$ pnictogen bonds at the equilibrium geometries.[a]

| $D_3Pn\cdots A^-$ | $\Delta E_{int}$ | $\Delta V_{elstat}$ | $\Delta E_{Pauli}$ | $\Delta E_{oi}$ | $\varepsilon(5a')$ | $\langle 5a'\|np_y\rangle$ | $\langle 5a'\|np_y\rangle^2$ | $\langle 4a'\|np_y\rangle$ | $Pop_{5a'}$ | $Pop_{npy}$ | $\Delta Q_{D_3Pn}^{VDD}$ |
|---|---|---|---|---|---|---|---|---|---|---|---|
| $F_3N\cdots F^-$ | –44.3 | –66.9 | 89.6 | –67.0 | –5.1 | 0.12 | 0.01 | 0.05 | 0.40 | 1.68 | –0.30 |
| $F_3N\cdots Cl^-$ | –4.3 | –5.8 | 4.5 | –3.1 | –0.2 | 0.10 | 0.01 | 0.05 | 0.02 | 1.99 | –0.01 |
| $F_3N\cdots Br^-$ | –3.5 | –4.7 | 3.5 | –2.3 | –0.1 | 0.10 | 0.01 | 0.04 | 0.02 | 2.00 | 0.00 |
| $Cl_3N\cdots F^-$ | –86.1 | –208.3 | 431.6 | –309.5 | –6.5 | 0.13 | 0.02 | 0.08 | 1.24 | 1.34 | –0.65 |
| $Cl_3N\cdots Cl^-$ | –28.5 | –41.8 | 69.2 | –55.9 | –5.2 | 0.11 | 0.01 | 0.06 | 0.54 | 1.59 | –0.36 |
| $Cl_3N\cdots Br^-$ | –9.7 | –11.9 | 18.8 | –16.7 | –3.7 | 0.09 | 0.01 | 0.03 | 0.26 | 1.75 | –0.18 |
| $Br_3N\cdots F^-$ | –83.3 | –204.1 | 439.6 | –318.8 | –6.0 | 0.12 | 0.01 | 0.07 | 1.25 | 1.38 | –0.67 |
| $Br_3N\cdots Cl^-$ | –10.0 | –10.3 | 19.2 | –18.9 | –3.6 | 0.08 | 0.01 | 0.04 | 0.23 | 1.86 | –0.18 |
| $Br_3N\cdots Br^-$ | –24.2 | –51.1 | 95.0 | –68.1 | –4.6 | 0.12 | 0.01 | 0.08 | 0.67 | 1.60 | –0.44 |
| $F_3P\cdots F^-$ | –66.4 | –167.7 | 221.7 | –120.3 | –2.1 | 0.15 | 0.02 | 0.19 | 0.28 | 1.75 | –0.35 |
| $F_3P\cdots Cl^-$ | –20.4 | –40.4 | 46.0 | –25.9 | –1.2 | 0.22 | 0.05 | 0.17 | 0.17 | 1.87 | –0.12 |
| $F_3P\cdots Br^-$ | –15.9 | –29.1 | 30.7 | –17.4 | –1.1 | 0.25 | 0.06 | 0.16 | 0.18 | 1.81 | –0.09 |
| $Cl_3P\cdots F^-$ | –99.3 | –222.6 | 312.1 | –188.7 | –4.1 | 0.16 | 0.03 | 0.13 | 0.48 | 1.70 | –0.52 |
| $Cl_3P\cdots Cl^-$ | –39.8 | –84.8 | 119.2 | –74.2 | –3.1 | 0.20 | 0.04 | 0.12 | 0.40 | 1.73 | –0.31 |
| $Cl_3P\cdots Br^-$ | –31.3 | –64.2 | 86.5 | –53.6 | –2.9 | 0.20 | 0.04 | 0.08 | 0.36 | 1.75 | –0.26 |
| $Br_3P\cdots F^-$ | –101.2 | –228.4 | 331.2 | –204.1 | –4.2 | 0.15 | 0.02 | 0.12 | 0.53 | 1.69 | –0.56 |
| $Br_3P\cdots Cl^-$ | –43.9 | –95.9 | 141.9 | –89.8 | –3.4 | 0.19 | 0.04 | 0.13 | 0.45 | 1.72 | –0.37 |
| $Br_3P\cdots Br^-$ | –35.3 | –73.7 | 104.8 | –66.5 | –3.2 | 0.20 | 0.04 | 0.12 | 0.42 | 1.72 | –0.32 |
| $F_3As\cdots F^-$ | –73.6 | –145.4 | 158.0 | –86.2 | –2.6 | 0.15 | 0.02 | 0.15 | 0.23 | 1.77 | –0.30 |
| $F_3As\cdots Cl^-$ | –34.9 | –64.4 | 67.6 | –38.1 | –2.2 | 0.21 | 0.04 | 0.16 | 0.20 | 1.84 | –0.17 |
| $F_3As\cdots Br^-$ | –29.0 | –52.1 | 52.8 | –29.7 | –2.1 | 0.22 | 0.05 | 0.16 | 0.18 | 1.85 | –0.14 |
| $Cl_3As\cdots F^-$ | –88.7 | –166.5 | 194.3 | –116.5 | –3.7 | 0.16 | 0.03 | 0.11 | 0.34 | 1.74 | –0.42 |
| $Cl_3As\cdots Cl^-$ | –46.4 | –85.5 | 101.9 | –62.8 | –3.2 | 0.21 | 0.04 | 0.11 | 0.33 | 1.76 | –0.29 |
| $Cl_3As\cdots Br^-$ | –39.7 | –71.4 | 83.2 | –51.5 | –3.1 | 0.22 | 0.05 | 0.10 | 0.31 | 1.78 | –0.26 |
| $Br_3As\cdots F^-$ | –88.8 | –167.8 | 203.9 | –124.9 | –3.7 | 0.15 | 0.02 | 0.11 | 0.37 | 1.75 | –0.45 |
| $Br_3As\cdots Cl^-$ | –47.6 | –89.9 | 112.3 | –70.1 | –3.3 | 0.20 | 0.04 | 0.11 | 0.35 | 1.78 | –0.33 |
| $Br_3As\cdots Br^-$ | –41.2 | –75.9 | 92.9 | –58.3 | –3.3 | 0.21 | 0.04 | 0.10 | 0.34 | 1.76 | –0.31 |
| $F_3Sb\cdots F^-$ | –80.8 | –148.9 | 143.6 | –75.5 | –3.0 | 0.16 | 0.03 | 0.15 | 0.20 | 1.82 | –0.31 |
| $F_3Sb\cdots Cl^-$ | –44.7 | –82.6 | 83.4 | –45.4 | –2.7 | 0.23 | 0.05 | 0.18 | 0.21 | 1.83 | –0.21 |
| $F_3Sb\cdots Br^-$ | –38.7 | –70.7 | 70.9 | –38.9 | –2.7 | 0.24 | 0.06 | 0.18 | 0.21 | 1.84 | –0.19 |
| $Cl_3Sb\cdots F^-$ | –89.4 | –158.0 | 161.0 | –92.4 | –3.4 | 0.16 | 0.03 | 0.11 | 0.26 | 1.79 | –0.38 |
| $Cl_3Sb\cdots Cl^-$ | –51.7 | –93.3 | 100.9 | –59.2 | –3.2 | 0.22 | 0.05 | 0.11 | 0.28 | 1.80 | –0.28 |
| $Cl_3Sb\cdots Br^-$ | –45.3 | –81.1 | 87.3 | –51.5 | –3.1 | 0.23 | 0.05 | 0.10 | 0.28 | 1.82 | –0.27 |
| $Br_3Sb\cdots F^-$ | –89.2 | –157.4 | 166.1 | –97.9 | –3.4 | 0.16 | 0.03 | 0.10 | 0.28 | 1.79 | –0.41 |
| $Br_3Sb\cdots Cl^-$ | –52.0 | –95.2 | 106.8 | –63.5 | –3.2 | 0.21 | 0.04 | 0.11 | 0.29 | 1.81 | –0.31 |
| $Br_3Sb\cdots Br^-$ | –45.8 | –83.2 | 92.7 | –55.3 | –3.2 | 0.22 | 0.05 | 0.11 | 0.30 | 1.81 | –0.30 |

[a] Computed at ZORA-M06/QZ4P; $\varepsilon(5a')$ = 5a' orbital energy of the prepared $D_3Pn$ fragment (in eV); $\langle\Phi|np\rangle$ = overlap between the $\Phi$ orbital of the $D_3Pn$ fragment (see Fig. 2) and one of the np orbitals of the halide $A^-$; Pop = Gross population (in electrons) of indicated orbital.

**Table S3.** Activation strain and energy decomposition analyses (in kcal mol$^{-1}$) of $D_mZ\cdots A^-$ hydrogen bonds, halogen bonds, chalcogen bonds, and pnictogen bonds at the equilibrium geometries.[a]

| $D_mZ\cdots A^-$ | $\Delta E$ | $\Delta E_{strain}$ | $\Delta E_{int}$ | $\Delta V_{elstat}$ | $\Delta E_{Pauli}$ | $\Delta E_{oi}$ |
|---|---|---|---|---|---|---|
| **FH···F$^-$** [b] | –45.8 | 22.1 | –67.9 | –76.2 | 72.9 | –64.6 |
| | | | | | | |
| **FF···F$^-$** [b] | –30.5 | 28.0 | –58.5 | –44.6 | 84.3 | –98.1 |
| **FCl···F$^-$** [b] | –52.3 | 14.0 | –66.4 | –94.5 | 124.9 | –96.7 |
| **FBr···F$^-$** [b] | –62.3 | 10.0 | –72.3 | –104.0 | 113.8 | –82.0 |
| **FI···F$^-$** [b] | –70.3 | 6.9 | –77.2 | –116.9 | 115.3 | –75.7 |
| | | | | | | |
| **$F_2O$···F$^-$** [b] | –21.9 | 28.3 | –50.2 | –55.3 | 87.5 | –82.4 |
| **$F_2S$···F$^-$** [b] | –50.1 | 16.2 | –66.3 | –126.5 | 168.3 | –108.1 |
| **$F_2Se$···F$^-$** [b] | –62.4 | 11.4 | –73.7 | –124.6 | 136.6 | –85.7 |
| **$F_2Te$···F$^-$** [b] | –72.4 | 7.9 | –80.3 | –134.6 | 132.8 | –78.6 |
| | | | | | | |
| **$F_3N$···F$^-$** | –11.8 | 32.5 | –44.3 | –66.9 | 89.6 | –67.0 |
| **$F_3P$···F$^-$** | –48.9 | 17.4 | –66.4 | –167.7 | 221.7 | –120.3 |
| **$F_3As$···F$^-$** | –61.0 | 12.6 | –73.6 | –145.4 | 158.0 | –86.2 |
| **$F_3Sb$···F$^-$** | –72.0 | 8.8 | –80.8 | –148.9 | 143.6 | –75.5 |

[a] Computed at ZORA-M06/QZ4P.

[b] Computed at ZORA-M06/QZ4P (from: L. de Azevedo Santos, T. A. Hamlin, T. C. Ramalho, F. M. Bickelhaupt, *ChemistryOpen*, 2021, **10**, 391–401).

**Table S4.** Cartesian coordinates, bonding energies (in kcal mol$^{-1}$) and the number of imaginary vibrational frequencies ($N_{imag}$) for all stationary points of $D_2N^{\cdot}$, $D_3N$ and $D_3N\cdots A^-$ structures, computed at ZORA-M06/QZ4P.

**$F_2N^{\cdot}$**
***E*** **=** -411.44
$N_{imag}$ = 0

| | | | |
|---|---|---|---|
| N | 0.000000 | 0.000000 | 0.282592 |
| F | 0.000000 | 1.045626 | -0.542918 |
| F | 0.000000 | -1.045626 | -0.542918 |

**$Cl_2N^{\cdot}$**
***E*** **=** -319.10
$N_{imag}$ = 0

| | | | |
|---|---|---|---|
| N | 0.000000 | 0.000000 | 0.205507 |
| Cl | 0.000000 | 1.390469 | -0.754532 |
| Cl | 0.000000 | -1.390469 | -0.754532 |

**$Br_2N^{\cdot}$**
***E*** **=** -297.35
$N_{imag}$ = 0

| | | | |
|---|---|---|---|
| N | 0.000000 | 0.000000 | 0.192269 |
| Br | 0.000000 | 1.524174 | -0.839361 |
| Br | 0.000000 | -1.524174 | -0.839361 |

**$F_3N$**
***E*** **=** -534.67
$N_{imag}$ = 0

| | | | |
|---|---|---|---|
| N | 0.000000 | 0.000000 | 0.431961 |
| F | -0.608092 | 1.053247 | -0.167194 |
| F | -0.608092 | -1.053247 | -0.167194 |
| F | 1.216184 | 0.000000 | -0.167194 |

**$Cl_3N$**
***E*** **=** -388.25
$N_{imag}$ = 0

| | | | |
|---|---|---|---|
| N | 0.000000 | 0.000000 | 0.436388 |
| Cl | -0.817370 | 1.415727 | -0.197496 |
| Cl | -0.817370 | -1.415727 | -0.197496 |
| Cl | 1.634740 | 0.000000 | -0.197496 |

**$Br_3N$**
***E*** **=** -361.45
$N_{imag}$ = 0

| | | | |
|---|---|---|---|
| N | 0.000000 | 0.000000 | 0.447775 |
| Br | -0.892970 | 1.546669 | -0.217524 |
| Br | -0.892970 | -1.546669 | -0.217524 |
| Br | 1.785940 | 0.000000 | -0.217524 |

**$F_3N\cdots F^-$**
***E*** **=** -683.28
$N_{imag}$ = 0

| | | | |
|---|---|---|---|
| N | 0.268143 | -0.004918 | 0.000000 |
| F | 0.361175 | 1.851683 | 0.000000 |
| F | -0.570517 | -0.034029 | 1.043030 |
| F | -0.570517 | -0.034029 | -1.043030 |
| F | 0.489462 | -1.850792 | 0.000000 |

**$Cl_3N\cdots F^-$**
***E*** **=** -555.49
$N_{imag}$ = 0

| | | | |
|---|---|---|---|
| N | 0.269408 | -0.613135 | 0.000000 |
| Cl | 0.696175 | 2.601343 | 0.000000 |
| Cl | -0.689932 | -0.238751 | 1.420412 |
| Cl | -0.689932 | -0.238751 | -1.420412 |
| F | 0.311517 | -2.028706 | 0.000000 |

**$Br_3N\cdots F^-$**
***E*** **=** -528.42
$N_{imag}$ = 0

| | | | |
|---|---|---|---|
| N | 0.308263 | -0.668113 | 0.000000 |
| Br | 0.753228 | 2.625398 | 0.000000 |
| Br | -0.767698 | -0.335662 | 1.564359 |
| Br | -0.767698 | -0.335662 | -1.564359 |
| F | 0.469481 | -2.070011 | 0.000000 |

**$F_3N\cdots Cl^-$**
***E*** **=** -654.46
$N_{imag}$ = 0

| | | | |
|---|---|---|---|
| N | 0.144541 | 0.589364 | 0.000000 |
| F | 0.167897 | 1.993453 | 0.000000 |
| F | -0.668004 | 0.358828 | 1.048791 |
| F | -0.668004 | 0.358828 | -1.048791 |
| Cl | 0.749892 | -2.592666 | 0.000000 |

**$Cl_3N\cdots Cl^-$**
***E*** **=** -511.08
$N_{imag}$ = 0

| | | | |
|---|---|---|---|
| N | 0.000000 | 0.000000 | 0.154715 |
| Cl | 0.000000 | -1.411055 | -0.891502 |
| Cl | 0.000000 | 1.411055 | -0.891502 |
| Cl | -2.230234 | 0.000000 | 0.823562 |
| Cl | 2.230234 | 0.000000 | 0.823562 |

**$Br_3N\cdots Cl^-$**
***E*** **=** -485.71
$N_{imag}$ = 0

| | | | |
|---|---|---|---|
| N | 0.125159 | 0.364584 | 0.000000 |
| Br | -0.902876 | -0.126707 | 1.559900 |
| Br | -0.902876 | -0.126707 | -1.559900 |
| Br | 0.189215 | 2.380353 | 0.000000 |
| Cl | 1.480533 | -2.100209 | 0.000000 |

**$F_3N\cdots Br^-$**

***E*** **=** -645.10

$N_{imag}$ **=** 0

| | | | |
|---|---|---|---|
| N | 0.028305 | 0.929630 | 0.000000 |
| F | 0.077148 | 2.324473 | 0.000000 |
| F | -0.787979 | 0.707762 | 1.049194 |
| F | -0.787979 | 0.707762 | -1.049194 |
| Br | 0.705095 | -2.487583 | 0.000000 |

**$Br_3N\cdots Br^-$**

***E*** **=** -475.97

$N_{imag}$ **=** 0

| | | | |
|---|---|---|---|
| N | 0.000000 | 0.000000 | 0.042993 |
| Br | 0.000000 | -1.583264 | -1.132542 |
| Br | 0.000000 | 1.583264 | -1.132542 |
| Br | -2.080213 | 0.000000 | 1.074513 |
| Br | 2.080213 | 0.000000 | 1.074513 |

**$Cl_3N\cdots Br^-$**

***E*** **=** -501.99

$N_{imag}$ **=** 0

| | | | |
|---|---|---|---|
| N | 0.137218 | -0.290134 | 0.000000 |
| Cl | -0.920571 | -0.347397 | 1.426909 |
| Cl | -0.920571 | -0.347397 | -1.426909 |
| Cl | 1.046788 | -1.960939 | 0.000000 |
| Br | 0.436098 | 2.614233 | 0.000000 |

**Table S5.** Cartesian coordinates, bonding energies (in kcal mol$^{-1}$) and the number of imaginary vibrational frequencies ($N_{imag}$) for all stationary points of $D_2P^{\bullet}$, $D_3P$ and $D_3P\cdots A^-$ structures, computed at ZORA-M06/QZ4P.

**$F_2P^{\bullet}$**
***E*** **=** -437.52
$N_{imag}$ = 0

| | | | |
|---|---|---|---|
| P | 0.000000 | 0.000000 | 0.449316 |
| F | 0.000000 | 1.193696 | -0.580018 |
| F | 0.000000 | -1.193696 | -0.580018 |

**$Cl_2P^{\bullet}$**
***E*** **=** -307.18
$N_{imag}$ = 0

| | | | |
|---|---|---|---|
| P | 0.000000 | 0.000000 | 0.488705 |
| Cl | 0.000000 | 1.588518 | -0.790998 |
| Cl | 0.000000 | -1.588518 | -0.790998 |

**$Br_2P^{\bullet}$**
***E*** **=** -276.17
$N_{imag}$ = 0

| | | | |
|---|---|---|---|
| P | 0.000000 | 0.000000 | 0.515621 |
| Br | 0.000000 | 1.721490 | -0.858336 |
| Br | 0.000000 | -1.721490 | -0.858336 |

**$F_3P$**
***E*** **=** -634.99
$N_{imag}$ = 0

| | | | |
|---|---|---|---|
| P | 0.000000 | 0.000000 | 0.598083 |
| F | -0.678515 | 1.175223 | -0.178630 |
| F | -0.678515 | -1.175223 | -0.178630 |
| F | 1.357030 | 0.000000 | -0.178630 |

**$Cl_3P$**
***E*** **=** -419.72
$N_{imag}$ = 0

| | | | |
|---|---|---|---|
| P | 0.000000 | 0.000000 | 0.711971 |
| Cl | -0.911235 | 1.578306 | -0.236744 |
| Cl | -0.911235 | -1.578306 | -0.236744 |
| Cl | 1.822470 | 0.000000 | -0.236744 |

**$Br_3P$**
***E*** **=** -370.81
$N_{imag}$ = 0

| | | | |
|---|---|---|---|
| P | 0.000000 | 0.000000 | 0.773113 |
| Br | -0.991177 | 1.716768 | -0.242240 |
| Br | -0.991177 | -1.716768 | -0.242240 |
| Br | 1.982353 | 0.000000 | -0.242240 |

**$F_3P\cdots F^-$**
***E*** **=** -820.73
$N_{imag}$ = 0

| | | | |
|---|---|---|---|
| P | 0.471584 | -0.045508 | 0.000000 |
| F | -0.575038 | -0.004777 | -1.220655 |
| F | -0.575038 | -0.004777 | 1.220655 |
| F | 0.260247 | -1.786014 | 0.000000 |
| F | 0.396623 | 1.706005 | 0.000000 |

**$Cl_3P\cdots F^-$**
***E*** **=** -623.93
$N_{imag}$ = 0

| | | | |
|---|---|---|---|
| P | 0.575347 | -0.103428 | 0.000000 |
| Cl | -0.764731 | -0.261293 | 1.612478 |
| Cl | -0.764731 | -0.261293 | -1.612478 |
| Cl | 0.171808 | 2.492628 | 0.000000 |
| F | 0.868878 | -1.726052 | 0.000000 |

**$Br_3P\cdots F^-$**
***E*** **=** -578.65
$N_{imag}$ = 0

| | | | |
|---|---|---|---|
| P | 0.625146 | -0.161380 | 0.000000 |
| Br | -0.819389 | -0.342368 | 1.744580 |
| Br | -0.819389 | -0.342368 | -1.744580 |
| Br | 0.235596 | 2.685646 | 0.000000 |
| F | 0.976812 | -1.759796 | 0.000000 |

**$F_3P\cdots Cl^-$**
***E*** **=** -767.30
$N_{imag}$ = 0

| | | | |
|---|---|---|---|
| P | 0.426576 | -0.301072 | 0.000000 |
| F | -0.607904 | -0.213195 | -1.190925 |
| F | -0.607904 | -0.213195 | 1.190925 |
| F | 0.370809 | -1.947454 | 0.000000 |
| Cl | 0.357187 | 2.397614 | 0.000000 |

**$Cl_3P\cdots Cl^-$**
***E*** **=** -561.45
$N_{imag}$ = 0

| | | | |
|---|---|---|---|
| P | 0.497391 | 0.133951 | 0.000000 |
| Cl | -0.816339 | -0.139683 | 1.601529 |
| Cl | -0.816339 | -0.139683 | -1.601529 |
| Cl | 0.123289 | 2.474218 | 0.000000 |
| Cl | 1.089662 | -2.161122 | 0.000000 |

**$Br_3P\cdots Cl^-$**
***E*** **=** -515.57
$N_{imag}$ = 0

| | | | |
|---|---|---|---|
| P | 0.568754 | 0.030817 | 0.000000 |
| Br | -0.856913 | -0.245260 | 1.737601 |
| Br | -0.856913 | -0.245260 | -1.737601 |
| Br | 0.212939 | 2.615147 | 0.000000 |
| Cl | 1.197970 | -2.193831 | 0.000000 |

**$F_3P\cdots Br^-$**

***E*** **=** -755.35

$N_{imag}$ **=** 0

| | | | |
|---|---|---|---|
| P | 0.413389 | -0.521103 | 0.000000 |
| F | -0.622566 | -0.471654 | -1.186509 |
| F | -0.622566 | -0.471654 | 1.186509 |
| F | 0.462055 | -2.151576 | 0.000000 |
| Br | 0.238774 | 2.456137 | 0.000000 |

**$Br_3P\cdots Br^-$**

***E*** **=** -501.72

$N_{imag}$ **=** 0

| | | | |
|---|---|---|---|
| P | 0.492980 | 0.160480 | 0.000000 |
| Br | -0.926680 | -0.132607 | 1.735107 |
| Br | -0.926680 | -0.132607 | -1.735107 |
| Br | 0.183894 | 2.691108 | 0.000000 |
| Br | 1.213018 | -2.285483 | 0.000000 |

**$Cl_3P\cdots Br^-$**

***E*** **=** -547.76

$N_{imag}$ **=** 0

| | | | |
|---|---|---|---|
| P | 0.409637 | 0.319838 | 0.000000 |
| Cl | -0.898438 | 0.032750 | 1.597765 |
| Cl | -0.898438 | 0.032750 | -1.597765 |
| Cl | 0.087809 | 2.614891 | 0.000000 |
| Br | 1.089627 | -2.206932 | 0.000000 |

**Table S6.** Cartesian coordinates, bonding energies (in kcal mol$^{-1}$) and the number of imaginary vibrational frequencies ($N_{imag}$) for all stationary points of $D_2As^{\cdot}$, $D_3As$ and $D_3As\cdots A^-$ structures, computed at ZORA-M06/QZ4P.

**$F_2As^{\cdot}$**
***E*** **=** -406.24
$N_{imag}$ = 0

| | | | |
|---|---|---|---|
| As | 0.000000 | 0.000000 | 0.523383 |
| F | 0.000000 | 1.291015 | -0.632746 |
| F | 0.000000 | -1.291015 | -0.632746 |

**$Cl_2As^{\cdot}$**
***E*** **=** -292.53
$N_{imag}$ = 0

| | | | |
|---|---|---|---|
| As | 0.000000 | 0.000000 | 0.549067 |
| Cl | 0.000000 | 1.667356 | -0.840659 |
| Cl | 0.000000 | -1.667356 | -0.840659 |

**$Br_2As^{\cdot}$**
***E*** **=** -264.06
$N_{imag}$ = 0

| | | | |
|---|---|---|---|
| As | 0.000000 | 0.000000 | 0.580135 |
| Br | 0.000000 | 1.795809 | -0.896786 |
| Br | 0.000000 | -1.795809 | -0.896786 |

**$F_3As$**
***E*** **=** -586.52
$N_{imag}$ = 0

| | | | |
|---|---|---|---|
| As | 0.000000 | 0.000000 | 0.678088 |
| F | -0.735339 | 1.273644 | -0.207718 |
| F | -0.735339 | -1.273644 | -0.207718 |
| F | 1.470677 | 0.000000 | -0.207718 |

**$Cl_3As$**
***E*** **=** -402.48
$N_{imag}$ = 0

| | | | |
|---|---|---|---|
| As | 0.000000 | 0.000000 | 0.761728 |
| Cl | -0.957050 | 1.657659 | -0.278656 |
| Cl | -0.957050 | -1.657659 | -0.278656 |
| Cl | 1.914100 | 0.000000 | -0.278656 |

**$Br_3As$**
***E*** **=** -357.61
$N_{imag}$ = 0

| | | | |
|---|---|---|---|
| As | 0.000000 | 0.000000 | 0.826786 |
| Br | -1.034028 | 1.790990 | -0.273400 |
| Br | -1.034028 | -1.790990 | -0.273400 |
| Br | 2.068057 | 0.000000 | -0.273400 |

**$F_3As\cdots F^-$**
***E*** **=** -784.31
$N_{imag}$ = 0

| | | | |
|---|---|---|---|
| As | 0.519932 | 0.140398 | 0.000000 |
| F | 0.137352 | 2.001938 | 0.000000 |
| F | -0.632615 | -0.006025 | 1.317394 |
| F | -0.632615 | -0.006025 | -1.317394 |
| F | 0.616005 | -1.757348 | 0.000000 |

**$Cl_3As\cdots F^-$**
***E*** **=** -609.25
$N_{imag}$ = 0

| | | | |
|---|---|---|---|
| As | 0.594428 | 0.012026 | 0.000000 |
| Cl | 0.276405 | 2.577110 | 0.000000 |
| Cl | -0.837011 | -0.229511 | 1.691083 |
| Cl | -0.837011 | -0.229511 | -1.691083 |
| F | 0.958406 | -1.802055 | 0.000000 |

**$Br_3As\cdots F^-$**
***E*** **=** -565.91
$N_{imag}$ = 0

| | | | |
|---|---|---|---|
| As | 0.703181 | -0.051608 | 0.000000 |
| Br | 0.295178 | 2.707101 | 0.000000 |
| Br | -0.808690 | -0.402281 | 1.819102 |
| Br | -0.808690 | -0.402281 | -1.819102 |
| F | 1.224672 | -1.819117 | 0.000000 |

**$F_3As\cdots Cl^-$**
***E*** **=** -731.50
$N_{imag}$ = 0

| | | | |
|---|---|---|---|
| As | 0.459413 | 0.275542 | 0.000000 |
| F | 0.217951 | 2.095210 | 0.000000 |
| F | -0.700949 | 0.135775 | 1.294282 |
| F | -0.700949 | 0.135775 | -1.294282 |
| Cl | 0.695304 | -2.308704 | 0.000000 |

**$Cl_3As\cdots Cl^-$**
***E*** **=** -553.88
$N_{imag}$ = 0

| | | | |
|---|---|---|---|
| As | 0.529968 | 0.132065 | 0.000000 |
| Cl | 0.280301 | 2.584045 | 0.000000 |
| Cl | -0.898392 | -0.144841 | 1.680286 |
| Cl | -0.898392 | -0.144841 | -1.680286 |
| Cl | 1.215379 | -2.235517 | 0.000000 |

**$Br_3As\cdots Cl^-$**
***E*** **=** -510.10
$N_{imag}$ = 0

| | | | |
|---|---|---|---|
| As | 0.649394 | 0.048438 | 0.000000 |
| Br | 0.289716 | 2.686734 | 0.000000 |
| Br | -0.855424 | -0.352654 | 1.811488 |
| Br | -0.855424 | -0.352654 | -1.811488 |
| Cl | 1.563182 | -2.211500 | 0.000000 |

**$F_3As\cdots Br^-$**

***E*** **=** -718.19

$N_{imag}$ **=** 0

| | | | |
|---|---|---|---|
| As | 0.424334 | 0.440561 | 0.000000 |
| F | 0.310043 | 2.257349 | 0.000000 |
| F | -0.741888 | 0.360472 | 1.290175 |
| F | -0.741888 | 0.360472 | -1.290175 |
| Br | 0.583429 | -2.375107 | 0.000000 |

**$Br_3As\cdots Br^-$**

***E*** **=** -497.12

$N_{imag}$ **=** 0

| | | | |
|---|---|---|---|
| As | 0.581753 | 0.122461 | 0.000000 |
| Br | 0.311113 | 2.742456 | 0.000000 |
| Br | -0.929011 | -0.251336 | 1.810385 |
| Br | -0.929011 | -0.251336 | -1.810385 |
| Br | 1.564658 | -2.321615 | 0.000000 |

**$Cl_3As\cdots Br^-$**

***E*** **=** -540.10

$N_{imag}$ **=** 0

| | | | |
|---|---|---|---|
| As | 0.452922 | 0.264327 | 0.000000 |
| Cl | 0.248881 | 2.692306 | 0.000000 |
| Cl | -0.975203 | -0.008603 | 1.677979 |
| Cl | -0.975203 | -0.008603 | -1.677979 |
| Br | 1.227408 | -2.288391 | 0.000000 |

**Table S7.** Cartesian coordinates, bonding energies (in kcal mol$^{-1}$) and the number of imaginary vibrational frequencies ($N_{imag}$) for all stationary points of $D_2Sb^{\cdot}$, $D_3Sb$ and $D_3Sb\cdots A^-$ structures, computed at ZORA-M06/QZ4P.

**$F_2Sb^{\cdot}$**
***E*** **=** -390.81
$N_{imag}$ = 0

| | | | |
|---|---|---|---|
| Sb | 0.000000 | 0.000000 | 0.567748 |
| F | 0.000000 | 1.403194 | -0.729636 |
| F | 0.000000 | -1.403194 | -0.729636 |

**$Cl_2Sb^{\cdot}$**
***E*** **=** -280.45
$N_{imag}$ = 0

| | | | |
|---|---|---|---|
| Sb | 0.000000 | 0.000000 | 0.611682 |
| Cl | 0.000000 | 1.772166 | -0.932213 |
| Cl | 0.000000 | -1.772166 | -0.932213 |

**$Br_2Sb^{\cdot}$**
***E*** **=** -252.20
$N_{imag}$ = 0

| | | | |
|---|---|---|---|
| Sb | 0.000000 | 0.000000 | 0.666436 |
| Br | 0.000000 | 1.899409 | -0.965193 |
| Br | 0.000000 | -1.899409 | -0.965193 |

**$F_3Sb$**
***E*** **=** -572.58
$N_{imag}$ = 0

| | | | |
|---|---|---|---|
| Sb | 0.000000 | 0.000000 | 0.722162 |
| F | -0.801030 | 1.387425 | -0.286157 |
| F | -0.801030 | -1.387425 | -0.286157 |
| F | 1.602060 | 0.000000 | -0.286157 |

**$Cl_3Sb$**
***E*** **=** -396.78
$N_{imag}$ = 0

| | | | |
|---|---|---|---|
| Sb | 0.000000 | 0.000000 | 0.813112 |
| Cl | -1.015350 | 1.758637 | -0.366356 |
| Cl | -1.015350 | -1.758637 | -0.366356 |
| Cl | 2.030699 | 0.000000 | -0.366356 |

**$Br_3Sb$**
***E*** **=** -352.22
$N_{imag}$ = 0

| | | | |
|---|---|---|---|
| Sb | 0.000000 | 0.000000 | 0.902866 |
| Br | -1.091026 | 1.889712 | -0.337508 |
| Br | -1.091026 | -1.889712 | -0.337508 |
| Br | 2.182051 | 0.000000 | -0.337508 |

**$F_3Sb\cdots F^-$**
***E*** **=** -781.38
$N_{imag}$ = 0

| | | | |
|---|---|---|---|
| Sb | 0.595336 | 0.184347 | 0.000000 |
| F | 0.052902 | 2.147485 | 0.000000 |
| F | -0.669109 | -0.004238 | 1.445482 |
| F | -0.669109 | -0.004238 | -1.445482 |
| F | 0.649524 | -1.851555 | 0.000000 |

**$Cl_3Sb\cdots F^-$**
***E*** **=** -610.69
$N_{imag}$ = 0

| | | | |
|---|---|---|---|
| Sb | 0.656380 | 0.111787 | 0.000000 |
| Cl | 0.171576 | 2.715889 | 0.000000 |
| Cl | -0.900766 | -0.152291 | 1.805164 |
| Cl | -0.900766 | -0.152291 | -1.805164 |
| F | 0.895401 | -1.890987 | 0.000000 |

**$Br_3Sb\cdots F^-$**
***E*** **=** -566.72
$N_{imag}$ = 0

| | | | |
|---|---|---|---|
| Sb | 0.734407 | 0.059751 | 0.000000 |
| Br | 0.237165 | 2.857815 | 0.000000 |
| Br | -0.915336 | -0.254475 | 1.931449 |
| Br | -0.915336 | -0.254475 | -1.931449 |
| F | 1.044699 | -1.930373 | 0.000000 |

**$F_3Sb\cdots Cl^-$**
***E*** **=** -727.75
$N_{imag}$ = 0

| | | | |
|---|---|---|---|
| Sb | 0.565157 | 0.283126 | 0.000000 |
| F | 0.124801 | 2.238750 | 0.000000 |
| F | -0.718724 | 0.095962 | 1.419111 |
| F | -0.718724 | 0.095962 | -1.419111 |
| Cl | 0.768715 | -2.351540 | 0.000000 |

**$Cl_3Sb\cdots Cl^-$**
***E*** **=** -555.78
$N_{imag}$ = 0

| | | | |
|---|---|---|---|
| Sb | 0.614244 | 0.148534 | 0.000000 |
| Cl | 0.156546 | 2.699643 | 0.000000 |
| Cl | -0.946801 | -0.154570 | 1.788222 |
| Cl | -0.946801 | -0.154570 | -1.788222 |
| Cl | 1.144570 | -2.388602 | 0.000000 |

**$Br_3Sb\cdots Cl^-$**
***E*** **=** -512.00
$N_{imag}$ = 0

| | | | |
|---|---|---|---|
| Sb | 0.712180 | 0.101959 | 0.000000 |
| Br | 0.217989 | 2.839521 | 0.000000 |
| Br | -0.937925 | -0.268048 | 1.916640 |
| Br | -0.937925 | -0.268048 | -1.916640 |
| Cl | 1.364108 | -2.394354 | 0.000000 |

**$F_3Sb\cdots Br^-$**

***E*** **=** -713.71

$N_{imag}$ **=** 0

| | | | |
|---|---|---|---|
| Sb | 0.533256 | 0.426676 | 0.000000 |
| F | 0.139622 | 2.383114 | 0.000000 |
| F | -0.755540 | 0.253135 | 1.414293 |
| F | -0.755540 | 0.253135 | -1.414293 |
| Br | 0.765369 | -2.403448 | 0.000000 |

**$Cl_3Sb\cdots Br^-$**

***E*** **=** -541.59

$N_{imag}$ **=** 0

| | | | |
|---|---|---|---|
| Sb | 0.593711 | 0.220878 | 0.000000 |
| Cl | 0.123130 | 2.754101 | 0.000000 |
| Cl | -0.963961 | -0.105965 | 1.784919 |
| Cl | -0.963961 | -0.105965 | -1.784919 |
| Br | 1.245475 | -2.481383 | 0.000000 |

**$Br_3Sb\cdots Br^-$**

***E*** **=** -497.77

$N_{imag}$ **=** 0

| | | | |
|---|---|---|---|
| Sb | 0.708896 | 0.154014 | 0.000000 |
| Br | 0.181578 | 2.869408 | 0.000000 |
| Br | -0.933794 | -0.252768 | 1.913972 |
| Br | -0.933794 | -0.252768 | -1.913972 |
| Br | 1.508974 | -2.494043 | 0.000000 |