On the physical nature of halogen bonds:

A QTAIM study

Olga A. SYZGANTSEVA, Vincent TOGNETTI, and Laurent JOUBERT

Normandy Univ., COBRA UMR 6014 & FR 3038, Université de Rouen, INSA Rouen, CNRS, 1 rue Tesnière 76821 Mont St Aignan, Cedex, France

Supplementary information
Contents

Figure S1. Views of all optimized structures ................................................................. 3
Figure S2. View of the optimized 1Bu complex.............................................................. 4
Graph S1. Variation of primary exchange interaction energies with respect to the corresponding delocalization indexes................................................................. 5
Table S1. Values for the secondary and primary interactions (in kcal/mol) for all complexes. 6
Table S2. Main properties for all X…D bond critical points........................................... 7
Figure S3. Atomic source contributions for all complexes.............................................. 8
Graph S2. Variation of binding energies with respect to the BCP_{X…D} density laplacian values. 9
Graph S3. Variation of binding energies with respect to the BCP_{X…D} energy densities........10
**Figure S1.** Views of all optimized structures (at the ωB97XD/aug-cc-pVTZ level). Color code: H in white, C in grey, F in pastel blue, Cl in green, Br in dark red, N in bright blue, O in bright red, S in yellow.
Figure S2. View of the $^1$Bu optimized complex (at the ωB97XD/aug-cc-pVTZ level). Color code: H in white, C in grey, Br in dark red, N in bright blue.
**Graph S1.** Variation of primary exchange interaction energies (in kcal/mol) with respect to the corresponding delocalization indexes.
| Compounds         | \(E_{\text{primary}}^{\text{QOA}}\) | \(E_{\text{primary}}^{\text{x}}\) | \(E_{\text{secondary}}^{\text{QOA}}\) | \(Df_{\text{primary}}\) | \(|\Delta q_{\text{CT}}|\) |
|-------------------|------------------------------------|----------------------------------|------------------------------------|--------------------------|--------------------------|
| CHBr···NH₃        | -41.1                              | -14.9                            | 19.3                               | 0.148                    | 0.028                    |
| CHBr···OH₂        | -38.0                              | -11.1                            | 21.6                               | 0.110                    | 0.010                    |
| CHBr···SH₂        | -10.5                              | -9.4                             | -3.4                               | 0.109                    | 0.008                    |
| CHBr···OH⁻        | -143.1                             | -68.1                            | 43.6                               | 0.568                    | 0.064                    |
| CHBr···OCH₂       | -35.2                              | -10.3                            | 17.8                               | 0.100                    | 0.007                    |
| CHCl···NH₃        | -10.9                              | -10.1                            | -3.9                               | 0.103                    | 0.019                    |
| CHCl···OH₂        | -6.8                               | -7.1                             | -3.4                               | 0.073                    | 0.006                    |
| CHCl···SH₂        | -6.5                               | -5.4                             | -2.1                               | 0.066                    | 0.005                    |
| CHCl···OH⁻        | -74.2                              | -42.3                            | 13.6                               | 0.373                    | 0.041                    |
| CHCl···OCH₂       | -4.9                               | -6.3                             | -7.5                               | 0.063                    | 0.003                    |
| CH₂Br···NH₃       | -9.2                               | -10.6                            | -6.5                               | 0.111                    | 0.016                    |
| CH₂Br···OH₂       | 0.1                                | -6.8                             | -10.1                              | 0.076                    | 0.002                    |
| CH₂Br···SH₂       | -7.6                               | -5.5                             | -3.5                               | 0.069                    | 0.008                    |
| CH₂Br···OH⁻       | -91.2                              | -50.3                            | 18.3                               | 0.443                    | 0.162                    |
| CH₂Br···OCH₂      | -0.2                               | -5.3                             | -12.8                              | 0.057                    | 0.007                    |
| FBr···NH₃         | -135.0                             | -60.0                            | 57.7                               | 0.498                    | 0.160                    |
| FBr···OH₂         | -107.7                             | -31.7                            | 66.3                               | 0.282                    | 0.057                    |
| FBr···SH₂         | -42.7                              | -44.1                            | -9.3                               | 0.426                    | 0.131                    |
| FBr···OH⁻         | -232.7                             | -126.3                           | 71.7                               | 0.952                    | 0.426                    |
| FBr···Br          | -107.3                             | -93.3                            | 19.9                               | 0.873                    | 0.419                    |
| FCl···NH₃         | -108.5                             | -56.2                            | 38.6                               | 0.459                    | 0.167                    |
| FCl···OH₂         | -83.5                              | -26.5                            | 50.1                               | 0.235                    | 0.052                    |
| FCl···SH₂         | -33.6                              | -35.5                            | -8.4                               | 0.345                    | 0.131                    |
| FCl···OH⁻         | -208.0                             | -144.8                           | 51.8                               | 1.023                    | 0.531                    |
| FCl···Br          | -101.6                             | -101.9                           | 11.5                               | 0.912                    | 0.502                    |
| ClBr···NH₃        | -77.0                              | -39.2                            | 24.6                               | 0.3436                   | 0.110                    |
| ClBr···OH₂        | -52.8                              | -20.0                            | 25.8                               | 0.1858                   | 0.032                    |
| ClBr···SH₂        | -25.7                              | -24.5                            | -5.5                               | 0.2528                   | 0.074                    |
| ClBr···OH⁻        | -235.8                             | -136.4                           | 62.6                               | 1.0106                   | 0.491                    |
| ClBr···Br          | -100.2                             | -96.7                            | 8.7                                | 0.8899                   | 0.066                    |
Table S2. Main properties (in atomic units) for all X…D bond critical points.

<table>
<thead>
<tr>
<th>Compounds</th>
<th>( \rho_c )</th>
<th>( \nabla^2 \rho_c )</th>
<th>( H_c )</th>
</tr>
</thead>
<tbody>
<tr>
<td>CHCBr···NH(_3)</td>
<td>0.0143</td>
<td>0.0470</td>
<td>0.0017</td>
</tr>
<tr>
<td>CHCBr···OH(_2)</td>
<td>0.0118</td>
<td>0.0459</td>
<td>0.0020</td>
</tr>
<tr>
<td>CHCBr···SH(_2)</td>
<td>0.0080</td>
<td>0.0242</td>
<td>0.0011</td>
</tr>
<tr>
<td>CHCBr···OH(^{-})</td>
<td>0.0642</td>
<td>0.1482</td>
<td>-0.0110</td>
</tr>
<tr>
<td>CHCBr···OCH(_2)</td>
<td>0.0120</td>
<td>0.0452</td>
<td>0.0019</td>
</tr>
<tr>
<td>CHCCI···NH(_3)</td>
<td>0.0102</td>
<td>0.0378</td>
<td>0.0020</td>
</tr>
<tr>
<td>CHCCI···OH(_2)</td>
<td>0.0079</td>
<td>0.0339</td>
<td>0.0019</td>
</tr>
<tr>
<td>CHCCI···SH(_2)</td>
<td>0.0048</td>
<td>0.0168</td>
<td>0.0011</td>
</tr>
<tr>
<td>CHCCI···OH(^{-})</td>
<td>0.0408</td>
<td>0.1360</td>
<td>0.0000</td>
</tr>
<tr>
<td>CHCCI···OCH(_2)</td>
<td>0.0080</td>
<td>0.0325</td>
<td>0.0017</td>
</tr>
<tr>
<td>CH(_2)CHBr···NH(_3)</td>
<td>0.0101</td>
<td>0.0328</td>
<td>0.0015</td>
</tr>
<tr>
<td>CH(_2)CHBr···OH(_2)</td>
<td>0.0070</td>
<td>0.0234</td>
<td>0.0010</td>
</tr>
<tr>
<td>CH(_2)CHBr···SH(_2)</td>
<td>0.0051</td>
<td>0.0153</td>
<td>0.0009</td>
</tr>
<tr>
<td>CH(_2)CHBr···OH(^{-})</td>
<td>0.0457</td>
<td>0.1301</td>
<td>-0.0024</td>
</tr>
<tr>
<td>CH(_2)CHBr···OCH(_2)</td>
<td>0.0067</td>
<td>0.0238</td>
<td>0.0011</td>
</tr>
<tr>
<td>FBr···NH(_3)</td>
<td>0.0549</td>
<td>0.1169</td>
<td>-0.0093</td>
</tr>
<tr>
<td>FBr···OH(_2)</td>
<td>0.0304</td>
<td>0.1113</td>
<td>0.0015</td>
</tr>
<tr>
<td>FBr···SH(_2)</td>
<td>0.0338</td>
<td>0.0699</td>
<td>-0.0028</td>
</tr>
<tr>
<td>FBr···OH(^{-})</td>
<td>0.1204</td>
<td>0.0937</td>
<td>-0.0607</td>
</tr>
<tr>
<td>FBr···Br(^{-})</td>
<td>0.0631</td>
<td>0.0630</td>
<td>-0.0145</td>
</tr>
<tr>
<td>FCl···NH(_3)</td>
<td>0.0546</td>
<td>0.1309</td>
<td>-0.0074</td>
</tr>
<tr>
<td>FCl···OH(_2)</td>
<td>0.0271</td>
<td>0.1095</td>
<td>0.0027</td>
</tr>
<tr>
<td>FCl···SH(_2)</td>
<td>0.0291</td>
<td>0.0711</td>
<td>-0.0009</td>
</tr>
<tr>
<td>FCl···OH(^{-})</td>
<td>0.1482</td>
<td>0.0597</td>
<td>-0.0788</td>
</tr>
<tr>
<td>FCl···Br(^{-})</td>
<td>0.0741</td>
<td>0.0738</td>
<td>-0.0182</td>
</tr>
<tr>
<td>ClBr···NH(_3)</td>
<td>0.0362</td>
<td>0.0968</td>
<td>-0.0014</td>
</tr>
<tr>
<td>ClBr···OH(_2)</td>
<td>0.0200</td>
<td>0.0749</td>
<td>0.0023</td>
</tr>
<tr>
<td>ClBr···SH(_2)</td>
<td>0.0196</td>
<td>0.0490</td>
<td>0.0004</td>
</tr>
<tr>
<td>ClBr···OH(^{-})</td>
<td>0.1309</td>
<td>0.0742</td>
<td>-0.0718</td>
</tr>
<tr>
<td>ClBr···Br(^{-})</td>
<td>0.0663</td>
<td>0.0614</td>
<td>-0.0157</td>
</tr>
</tbody>
</table>
Figure S3. Atomic source contributions for all complexes.
Graph S2. Variation of binding energies (in kcal/mol) with respect to the BCP$_{X...D}$ density laplacian values (in atomic units).

\[ E_{\text{DFT}}^{\text{bind}} \quad v^2 \rho \quad E_{\text{IQA}}^{\text{inter}} \quad v^2 \rho \]
Graph S3. Variation of binding energies (in kcal/mol) with respect to the BCP_{X...D} density energies (in atomic units).