# Supporting Information

*Brandon Watson, Olivia Grounds, William Borley, Sergiy V. Rosokha*¹

**Resolving Halogen vs Hydrogen Bonding Dichotomy in Solutions: Intermolecular Complexes of Trihalomethanes with Halide and Pseudohalide Anions**

Department of Chemistry, Ball State University, Muncie, IN, USA, 47306

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¹ Corresponding author, e-mail: svrosokha@bsu.edu, phone: +1-765-285-8615.
Calculation of the equilibria constants

Formation constants of the XB and/or HB complexes \([\text{CHX}_3, \text{A}^-]\) \((X = \text{Cl}, \text{Br}, \text{I}; A = \text{Cl}, \text{Br}, \text{I}, \text{NCS}, \text{NCO}, \text{N}_3)\) were established via UV-Vis and NMR measurements of the acetonitrile solutions containing constant concentrations (from 2 to 5 mM) of CHX\(_3\) and variable concentrations (from 0 to ~ 0.4M) of tetrapropylammonium salts of (pseudo-)halide anions, \(\text{A}^-\).\(^2\) Several series of measurements were also done with n-Bu\(_4\)NA salts, and they afforded the same, within accuracy limit, formation constants as the corresponding measurements with Pr\(_4\)NA.\(^3\) For the UV-Vis experiments, 10.0 mL of a stock solution of CHX\(_3\) (10.0 mM) and 5.00 mL of solution of Pr\(_4\)NA (from 0.4 M to 0.8 M) were typically prepared. Then, 0.500 mL of the stock solution of CHX\(_3\) were mixed in a microvolumetric (1.00 mL) flask with \(x\) mL of stock solution of Pr\(_4\)NA and \((0.500-x)\) mL of acetonitrile (where \(x\) typically were 0.500, 0.400, 0.330, 0.250, 0.200, 0.160, 0.130, 0.100, 0.080, 0.065, 0.050, 0.035, 0.020 or similar numbers) using gas-tight microsyringes with capacities from 0.050 mL to 0.500 mL. UV-Vis measurements were carried out in acetonitrile at 22 °C using quartz (1-mm path length) spectroscopic cells on a CARY 500 spectrophotometer. A Dewar equipped with quartz lens was used for the measurements at +5 to -70 °C. The temperature was adjusted with an ethanol-liquid nitrogen bath (±0.5 K). Solutions of for the NMR measurements were prepared in a similar way. However, stock solutions of CHX\(_3\) (10.0 mM, 5.00 mL) and (Pr\(_4\)NA 3 mL, from 0.4 M to 0.8 M) for NMR measurements were prepared in CD\(_3\)CN (containing internal TMS standard). Also, 0.250 mL of solution of CHX\(_3\) were mixed with \(x\) mL Pr\(_4\)NA and \((0.250-x)\) mL of CD\(_3\)CN, so the total volumes of solutions for NMR measurements were 0.5 mL. \(^1\)H NMR measurements were performed on the 400 MHz NMR-ECZ400S spectrometer at 22 °C.

Alternatively, series of UV-Vis measurements were done by mixing 0.250 mL of the stock solution of CHX\(_3\) (prepared as described above) with 0.250 mL of the stock solution of Pr\(_4\)NA in Teflon-capped (1 mm) cuvettes equipped with sidearm. Separately, 5.0 mL of the stock solution of CHX\(_3\) was mixed with 5.0 mL of acetonitrile (so the concentration of the CHX\(_3\) in this solution was the same as that in the cuvette). After first spectrum was measured, \(x\) mL portions of the diluted solution of CHX\(_3\) (where \(x = 0.125, 0.150, 0.200, 0.250, 0.300, 0.400, 0.500, 0.600, 0.750, 0.900, 1.000, 1.500, 2.000\) or similar number) were added progressively and the spectra were measured after each addition. Thus, regardless of the method of preparation of solutions for the UV-Vis and NMR measurements, the concentrations of CHX\(_3\) were kept constant, and concentrations of Pr\(_4\)NA varied substantially in a series of measurements; and the values of formation constants derived from both types of the UV-Vis experiments were the same (within the accuracy limit).

\(^2\) Specific concentration of CHX\(_3\) and Pr\(_4\)NA salts for different donor/acceptor pairs are listed in figure captures (see Figure 1, Figure S1 – S6, S9)

\(^3\) Control experiments with tetrapropylammonium tetrafluoroborate verified that variation of concentration of this non-bonding anion in its mixtures with trihalomethanes in acetonitrile has negligible effects (as compared to that of pseudo-halide anions) on the chemical shifts of the CHX\(_3\) protons (see Figure 2).
The formation constants and spectral characteristics obtained (as in the earlier studies) assuming formation of only one type of complex represent average values from 3-5 series of UV-Vis or NMR experiments for each CHX₃/A’ pair. Each of such series typically included 8-10 points. UV-Vis absorption values measured at two wavelengths were normally used in the calculations. For the multivariable treatments of the UV and NMR data, the data from 2-3 series of measurements of each CHX₃/A pair (with the same concentration of trihalomethane) were combined and treated simultaneously.

Extinction coefficients ε for [CHX₃,A] complexes, limiting proton NMR shifts and equilibrium constants of their formation, K_UV\text{eff} and K_NMR\text{eff}, (Table 1 and Table S1) were first calculated via the Benesi-Hildebrand procedure and, additionally, via regression analysis. These treatments were based, as in the previous studies, on the assumption that only one type (either XB or HB) of 1:1 complex is formed in solution, i.e. that the formation of other types of complexes can be neglected:

\[
\text{CHX}_3 + A^- \xrightleftharpoons{} K_{\text{eff}} [\text{CHX}_3, A^-] \tag{S1}
\]

The effective formation constant of the complex is expressed as

\[
K_{\text{eff}} = \frac{C_{\text{com}}}{((C^o_D - C_{\text{com}})(C^o_A - C_{\text{com}}))} \tag{S2}
\]

where C_{\text{com}} is the concentration of the complex, and C^o_D and C^o_A are initial concentrations of CHX₃ and A’, respectively. When C^o_A >> C^o_D, C^o_A - C_{\text{com}} \approx C^o_A. Therefore

\[
K_{\text{eff}}(C^o_D - C_{\text{com}})C^o_A - C_{\text{com}} = 0 \tag{S3}
\]

Or

\[
C_{\text{com}} = \frac{K_{\text{eff}}C^o_D C^o_A}{((K_{\text{eff}})^{-1}+1)} \tag{S4}
\]

Taking into account that: ΔAbs = ε I C_{\text{com}} where ΔAbs is the absorbance of the complex at certain wavelength (obtained by subtraction of the absorption of components), and I is the length of the spectrophotometric cell, the latter can be rearranged as the Benesi-Hildebrand equation:

\[
C^o_D/\Delta\text{Abs} = 1/\varepsilon \cdot \frac{1}{I} + \left\{1/\left( \frac{K_{\text{UV\text{eff}}} \cdot \varepsilon \cdot I}{C^o_A} \right) \right\} \times 1/[\ C^o_A] \tag{S5}
\]

The Benesi-Hildebrand treatments of the UV-Vis absorption data are illustrated below in Figures S1C-S6C. It should be noted that the Benesi-Hildebrand procedure provided reliable results only if one reactant is present in a great excess and the complexation of the other reactant (in deficit) is in the 20-80% range (which is difficult to obtain with K values of ~ 1 or less due to solubility limitations). Thus, to verify the values of K_UV\text{eff} and ε, as well as to determine K_NMR\text{eff} and Δδ_ε, we carried out regression analysis of the UV-Vis and NMR data without assumptions made in the Benesi-Hildebrand method. In this case, solving equation S2 leads to:

\[
C_{\text{com}} = (C^o_A + C^o_D + 1/K_{\text{eff}}) + \sqrt{(\frac{C^o_A + C^o_D + 1/K_{\text{eff}}}{2})^2 - 4C^o_A C^o_D ^{0.5}}/2 \tag{S6}
\]

So, changes in the UV-Vis absorption intensity and shift of the proton signal can be expressed as:

\[
\Delta\text{Abs} = \varepsilon I C_{\text{com}} = \varepsilon I \times \{(C^o_A + C^o_D + 1/K_{\text{eff}}) - ((C^o_A + C^o_D + 1/K_{\text{eff}})^2 - 4C^o_A C^o_D ^{0.5})/2 \tag{S7}
\]\n
\[
\Delta\delta = \Delta\delta_\varepsilon C_{\text{com}}/C^o_D = (\Delta\delta_\varepsilon/C^o_D)\times \{(C^o_A + C^o_D + 1/K_{\text{eff}}) - ((C^o_A + C^o_D + 1/K_{\text{eff}})^2 - 4C^o_A C^o_D ^{0.5})/2 \tag{S8}
\]
where \( \varepsilon \) and \( l \) are extinction coefficient of the complex and the length of the cell which was used in the UV-Vis measurements, and \( \Delta \delta_x = \delta_x - \delta_0 \) is the difference between the ppm of the CHX\(_3\) proton in the presence of the infinite concentration of anion, \( \delta_x \) (i.e. when all CHX\(_3\) molecules are bonded to anions) and that of the separate CHX\(_3\), \( \delta_0 \). The fitting of the results of the UV-Vis titrations to eqs S7 (with \( \varepsilon \) and \( K_{\text{UV}}^{\text{eff}} \) as the adjustable parameters) using the Origin Pro 2016 are illustrated in Figures S1D-S6D. They produced values of \( K_{\text{UV}}^{\text{eff}} \) and \( \varepsilon \) in Table S1. (These values were consistent with those obtained via the Benesi-Hildebrandt treatment). The fitting of the results of NMR experiments (with \( K_{\text{NMR}}^{\text{eff}} \) and \( \Delta \delta_x \) as adjustable parameters) are illustrated in Figures S9 – S11. They produced the values of \( K_{\text{NMR}}^{\text{eff}} \) and \( \Delta \delta_x \) in Table S1.

The spectral and computational data indicated, however, that interaction of trihalomethanes with nucleophile \( A^- \) resulted in formation of both XB and HB complexes. These processes are characterized by equilibria constants \( K_{\text{XB}} \) and \( K_{\text{HB}} \), respectively (eqs S9 and S10):

\[
\begin{align*}
\text{CHX}_3 + A^- & \xrightarrow{K_{\text{XB}}} [\text{X}_2\text{HC-X} - \text{X}^\bullet \bullet \text{-A}^-] \\
\text{CHX}_3 + A^- & \xrightarrow{K_{\text{HB}}} [\text{X}_3 \text{C-H} - \text{X}^\bullet \bullet \text{-A}^-]
\end{align*}
\]

Analysis of the experimental data pointed out that interaction of trihalomethanes with anions produces under conditions of experiments predominantly 1:1 complexes (either XB or HB).\(^4\) Their formation constants of the latter are expressed as:

\[
\begin{align*}
K_{\text{XB}} &= C_{\text{XB}} / (((C_{\text{D}}^0 - C_{\text{XB}} - C_{\text{HB}})(C_{\text{A}}^0 - C_{\text{XB}} - C_{\text{HB}})) ) \\
K_{\text{HB}} &= C_{\text{HB}} / (((C_{\text{D}}^0 - C_{\text{XB}} - C_{\text{HB}})(C_{\text{A}}^0 - C_{\text{XB}} - C_{\text{HB}})) )
\end{align*}
\]

where \( C_{\text{XB}} \) and \( C_{\text{HB}} \) are equilibria concentrations of the XB and HB complexes. Eqs S11 and S12 can be rearranged as:

\[
\begin{align*}
K_{\text{XB}}((C_{\text{D}}^0 - C_{\text{XB}} - C_{\text{HB}})(C_{\text{A}}^0 - C_{\text{XB}} - C_{\text{HB}})) &= C_{\text{XB}} \\
K_{\text{HB}}((C_{\text{D}}^0 - C_{\text{XB}} - C_{\text{HB}})(C_{\text{A}}^0 - C_{\text{XB}} - C_{\text{HB}})) &= C_{\text{HB}}
\end{align*}
\]

Thus

\[
\begin{align*}
(C_{\text{D}}^0 - C_{\text{XB}} - C_{\text{HB}})(C_{\text{A}}^0 - C_{\text{XB}} - C_{\text{HB}}) &= C_{\text{XB}}/K_{\text{XB}} \\
(C_{\text{D}}^0 - C_{\text{XB}} - C_{\text{HB}})(C_{\text{A}}^0 - C_{\text{XB}} - C_{\text{HB}}) &= C_{\text{HB}}/K_{\text{HB}}
\end{align*}
\]

Or

\[
\begin{align*}
C_{\text{HB}} / K_{\text{HB}} &= C_{\text{XB}} / K_{\text{XB}} \\
C_{\text{XB}} &= K_{\text{XB}} C_{\text{HB}} / K_{\text{HB}}
\end{align*}
\]

\(^4\) This conclusion is based on the observation that the Jobs plot (for both CHI\(_3\) in the current work and CHBr\(_3\) in the reported earlier data) shows the formation of 1:1 complex. Apparently, polarization of the CHX\(_3\) molecule hinders the binding of the second anion (and this applies to both modes of interaction). Moreover, the fitting of the experimental data using the model in which XB and HB modes do not affect each other, i.e. \( C_{\text{XB}} = K_{\text{XB}}((C_{\text{D}}^0 - C_{\text{XB}} - C_{\text{HB}})(C_{\text{A}}^0 - C_{\text{XB}} - C_{\text{HB}})) \) and \( C_{\text{HB}} = K_{\text{HB}}((C_{\text{D}}^0 - C_{\text{XB}} - C_{\text{HB}})(C_{\text{A}}^0 - C_{\text{XB}} - C_{\text{HB}})) \) either failed to converge or produced unsatisfactory results (see Figure S12). Finally, the calculated free energies of formation of the triple \([\text{A}...\text{H CX}_3...\text{A}^-]\) complexes (in which one anion is XB bonded and another is HB bonded to the same CHX\(_3\) molecule) were \( \approx 6 \text{ kcal/mol} \) more positive than that of the XB or HB dyads. So, the ratio of concentrations of triple to double complexes \( C_T / C_D = (K_T/C_D^2)(K_D/C_D/C_A) = \exp(-\Delta \Delta G/RT) \times C_A \) (where \( K_T \) is a formation constant of the triple complex, and \( K_D \) is a formation constant of the XB or HB complex, and \( \Delta \Delta G \) is the difference between free energies of their formations). Since \( C_A < 1 \text{ M} \) and \( \exp(-\Delta \Delta G/RT) \approx \exp(-6/0.6) \approx 4.5 \times 10^{-5} \), the \( C_T < C_D \times 10^{-4} \) and can thus formation of triple complexes can be neglected.
\[ C_{HB} = K_{HB}C_{XB}/K_{XB} \]  \hspace{1cm} (S19)

Substitution of \( C_{HB} \) in eq S15 (using eq S19) and rearrangements leads to the quadratic equation:

\[
(C_0^D - C_{XB}(1+K_{HB}/K_{XB}))(C_0^A - C_{XB}(1+K_{HB}/K_{XB})) - C_{XB}/K_{XB} = 0 \hspace{1cm} (S20)
\]

\[
C_0^AC_0^D/(1 + K_{HB}/K_{XB}) - C_{XB} (C_0^A + C_0^D + 1/(K_{XB}+K_{HB})) + C_{XB}^2(1 + K_{HB}/K_{XB}) = 0 \hspace{1cm} (S21)
\]

Thus:

\[
C_{XB} = ((C_0^A+C_0^D+1/(K_{XB}+K_{HB})) - (C_0^A+C_0^D+1/(K_{XB}+K_{HB}))^2 - 4C_0^AC_0^D)^{0.5})/(2(1+K_{HB}/K_{XB})) \hspace{1cm} (S22)
\]

In a similar way:

\[
C_{HB} = ((C_0^A+C_0^D+1/(K_{XB}+K_{HB})) - (C_0^A+C_0^D+1/(K_{XB}+K_{HB}))^2 - 4C_0^AC_0^D)^{0.5})/(2(1+K_{HB}/K_{HB})) \hspace{1cm} (S23)
\]

As such, \( \Delta Abs = \varepsilon \times C_{XB} \)

\[
\Delta \delta = \Delta \delta_{XB}/C_0^D \times C_{XB} + \Delta \delta_{HB}/C_0^D \times C_{HB} =
\]

\[
= \Delta \delta_{XB}/C_0^D \times ((C_0^A+C_0^D+1/(K_{XB}+K_{HB})) - (C_0^A+C_0^D+1/(K_{XB}+K_{HB}))^2 - 4C_0^AC_0^D)^{0.5})/(2(1+K_{HB}/K_{XB}))
\]

\[
+ \Delta \delta_{HB}/C_0^D \times ((C_0^A+C_0^D+1/(K_{XB}+K_{HB})) - (C_0^A+C_0^D+1/(K_{XB}+K_{HB}))^2 - 4C_0^AC_0^D)^{0.5})/(2(1+K_{XB}/K_{HB})) \hspace{1cm} (S25)
\]

Simultaneous fitting of the dependencies of \( \Delta Abs \) and \( \Delta \delta \) on concentration of \( A^- \) using eqs S24 and S25 (multivariable non-linear fitting option in Origin Pro 2016) are illustrated in Figures S13 – S19 (Table S4). In these fitting, the concentration of anion \([A^-]\) was independent variable, values of \( \Delta Abs \) and \( \Delta \delta \) were two dependent variables, \( K_{HB}, K_{XB} \) and \( \varepsilon \) were adjustable parameters, and \( \Delta \delta_{XB} \) and \( \Delta \delta_{HB} \) (taken from computations) and concentration of CHX3 were constant. Such fittings produced values of \( K_{XB} \) and \( K_{HB} \).

It should be noted that the dependences of the values of \( \Delta Abs \) and \( \Delta \delta \) on \( C_0^A \) (at constant \( C_0^D \)) with five adjustable parameters \((K_{HB}, K_{XB}, \Delta \delta_{XB}, \Delta \delta_{HB} \) and \( \varepsilon \)) produced unreliable results with the standard errors higher than 100%.

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5 The simultaneous fitting of the dependencies of \( \Delta Abs \) and \( \Delta \delta \) on \( C_0^A \) (at constant \( C_0^D \)) with five adjustable parameters \((K_{HB}, K_{XB}, \Delta \delta_{XB}, \Delta \delta_{HB} \) and \( \varepsilon \)) produced unreliable results with the standard errors higher than 100%. 
Figure S1. A) UV-Vis spectra of solutions with constant concentration of CHI₃ (1.1 mM) and various concentrations of Pr₄NBr salt in acetonitrile. The solid black line and dashed red line represent spectra of solutions of individual CHI₃ (1.1 mM) and Pr₄NBr (222 mM), respectively. Concentration of Pr₄NBr (solid lines, from bottom to top): 0 mM, 8.8 mM, 17.8 mM, 31.0 mM, 44.4 mM, 66.6 mM, 93.2 mM, 119.8 mM, and 133.1 mM. B) Differential absorption spectra obtained by subtraction of the absorption of components from the spectra of the mixtures representing absorption spectra of the [CHI₃, Br⁻] complexes. C) Benesi-Hildebrand treatment of absorption data. D) Fitting of the ΔAbs to eq S7 (i.e. assuming one complex formation). E) Deconvolution of the absorption of the [CHI₃, Br⁻] complex into Gaussian components.
Figure S2. A) UV-Vis spectra of solutions with constant concentration of CHI₃ (1.1 mM) and various concentrations of Pr₄NN₃ salt in acetonitrile. The solid black line and dashed red line represent spectra of solutions of individual CHI₃ (1.1 mM) and Pr₄NBr (249 mM), respectively. Concentration of Pr₄NN₃ (solid lines, from bottom to top): 0 mM, 6.4 mM, 22.2 mM, 31.8 mM, 47.6 mM, 63.5 mM, 95.3 mM, and 158.8 mM. B) Differential absorption spectra obtained by subtraction of the absorption of components from the spectra of the mixtures representing absorption spectra of the [CHI₃, N₃⁻] complexes. C) Benesi-Hildebrand treatment of absorption data. D) Fitting of the ΔAbs to eq S7 (i.e. assuming one complex formation). E) Deconvolution of the absorption of the [CHI₃, N₃⁻] complex into Gaussian components.
**Figure S3.** A) UV-Vis spectra of solutions with constant concentration of CHI₃ (1.1 mM) and various concentrations of Pr₄NCl salt in acetonitrile. The solid black line and dashed red line represent spectra of solutions of individual CHI₃ (1.1 mM) and Pr₄NCl (255 mM), respectively. Concentration of Cl⁻ (solid lines, from bottom to top): 0 mM, 10 mM, 20 mM, 36 mM, 51 mM, 77 mM, 102 mM, 153 mM, and 255 mM. B) Differential absorption spectra obtained by subtraction of the absorption of components from the spectra of the mixtures representing absorption spectra of the [CHI₃, Cl⁻] complexes. C) Benesi-Hildebrand treatment of absorption data. D) Fitting of the ∆Abs to eq S7 (i.e. assuming one complex formation). E) Deconvolution of the absorption of the [CHI₃, Cl⁻] complex into Gaussian components.
**Figure S4.** A) UV-Vis spectra of solutions with constant concentration of CHI₃ (1.1 mM) and various concentrations of Pr₄NI salt in acetonitrile. The solid black line and dashed red line represent spectra of solutions of individual CHI₃ (1.1 mM) and Pr₄NI (252 mM), respectively. Concentration of I⁻ (solid lines, from bottom to top): 0 mM, 10.1 mM, 35.2 mM, 50.4 M, 75.5 mM, 100.7 mM, 151.1 mM, and 251.8 mM. B) Differential absorption spectra obtained by subtraction of the absorption of components from the spectra of the mixtures representing absorption spectra of the [CHI₃, I⁻] complexes. C) Benesi-Hildebrand treatment of absorption data. D) Fitting of the Δ Abs to eq S7 (i.e. assuming one complex formation). E) Deconvolution of the absorption of the [CHI₃, I⁻] complex into Gaussian components.
Figure S5. A) UV-Vis spectra of solutions with constant concentration of CHI₃ (1.1 mM) and various concentrations of Pr₄NNCS salt in acetonitrile. The solid black line and dashed red line represent spectra of solutions of individual CHI₃ (1.1 mM) and Pr₄NNCS (255 mM), respectively. Concentration of NCS⁻ (solid lines, from bottom to top): 0 mM, 8.8 mM, 17.6 mM, 30.8 mM, 44.1 mM, 66.1 mM, 132.2 mM, and 220.3 mM. B) Differential absorption spectra obtained by subtraction of the absorption of components from the spectra of the mixtures representing absorption spectra of the [CHI₃, NCS⁻] complexes. C) Benesi-Hildebrand treatment of absorption data. D) Fitting of the ΔAbs to eq S7 (i.e. assuming one complex formation). E) Deconvolution of the absorption of the [CHI₃, NCS⁻] complex into Gaussian components.
Figure S6. A) UV-Vis spectra of solutions with constant concentration of CHI₃ (1.1 mM) and various concentrations of Bu₄NNCO salt in acetonitrile. The solid black line and dashed red line represent spectra of solutions of individual CHI₃ (1.1 mM) and Bu₄NNCO (249 mM), respectively. Concentration of Bu₄NNCO (solid lines, from bottom to top): 0 mM, 3.1 mM, 6.2 mM, 10.9 mM, 15.5 mM, 23.3 mM, 3.1 mM, 46.6 mM and 77.6 mM. B) Differential absorption spectra obtained by subtraction of the absorption of components from the spectra of the mixtures representing absorption spectra of the [CHI₃, NCO⁻] complexes. C) Benesi-Hildebrand treatment of absorption data. D) Fitting of the ∆Abs to eq S7 (i.e. assuming one complex formation). E) Deconvolution of the absorption of the [CHI₃, NCO⁻] complex into Gaussian components.
Figure S7. Job’s plot: dependence of ΔAbs on the molar fraction of bromide for the solution containing CHI₃ and Br⁻ with constant sum of the concentration of components (20 mM) on fraction of Br⁻ (taken as a salt with Pr₄N⁺ counter-ion). Blue and orange points show absorption measured at λ = 340 nm and λ = 296 nm, respectively.

Figure S8. (A) Correlation between the energies of the absorption bands of the [CHX₃, A⁻] complexes (CHI₃ (0) or CHBr₃ (4)) and the HOMO energies of A⁻ anions: N₃⁻ (1), I⁻ (2), NCS⁻ (3), Br⁻ (4), NCO⁻ (5), Cl⁻ (6)). B) Mulliken correlation between the energies of the lowest-energy bands of the complexes of bromosubstituted electrophiles and anions, [R-Br, A⁻] and the difference of their frontier orbital energies. Complexes of CHBr₃ are shown as red circles. HOMO/LUMO energies (from mp2/6-311G**/SCIPCM computations) and wavelengths are listed below (from refs 50-52).

<table>
<thead>
<tr>
<th>R-Br</th>
<th>E(LUMO)</th>
<th>Br⁻</th>
<th>Cl⁻</th>
<th>I⁻</th>
<th>NCS⁻</th>
<th>NCO⁻</th>
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<td>265</td>
<td>345</td>
<td>315</td>
<td>274</td>
<td>338</td>
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<tr>
<td>CHBr₃</td>
<td>0.07564</td>
<td>259</td>
<td>294</td>
<td>275</td>
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<td>CBr₃CN</td>
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<td>285</td>
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<td>308</td>
<td>266</td>
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<td>CBr₃COOH</td>
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<td>289</td>
<td>238</td>
<td>300</td>
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<td>247</td>
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<td>308</td>
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<tr>
<td>CBr₃COF₂₆</td>
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<tr>
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<td>327</td>
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<td>-0.26925</td>
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Figure S9. Results of the $^1$H NMR measurements of solutions with constant concentration of CH$_3$I (5.1 mM) and variable concentrations of with $\Lambda$ anions (as indicated) (CD$_3$CN, 22°C) and their fitting using eq S8. Note, the combined results of 2-3 independent series for each pair are shown; anions were taken as Pr$_4$NA salts.
Figure S10. Spectra of solutions with constant concentration of CHBr₃ (5.0 mM) and various concentrations of Pr₄NI (solid lines from the bottom to the top: 0, 13.7, 27.4, 45.6, 63.9, 82.2, 110, 128, 146, 164, 183, 201 and 228 mM). Spectrum of the separate 200 mM solution of Pr₄NI is shown as a dashed line. Insert: Spectra obtained by subtraction of the absorption of components from the spectra of their mixtures.

Figure S11. Results of the ¹H NMR measurements of solutions with constant concentration of CHBr₃ (5.0 mM) and variable concentrations of A⁻ anions (as indicated) (CD₃CN, 22⁰C) and their fitting using eq S8. Note, the combined results of 2-3 independent series for each pair are shown; anions were taken as Pr₄NA salts.
Figure S12. Results of the $^1$H NMR measurements of solutions with constant concentration of CHCl$_3$ (5.1 mM) and variable concentrations of A$^-$ anions (as indicated) (CD$_3$CN, 22°C) and their fitting using eq S8. Note, the combined results of 2-3 independent series for each pair are shown; anions were taken as Pr$_4$NA salts.
**Table S1.** Effective formation constants of \([\text{CHX}_3, \text{A}^-]\) complexes.\(^a\)

<table>
<thead>
<tr>
<th>CHX(_3)</th>
<th>A(^-)</th>
<th>(K_{\text{UV}}^{\text{eff}}, \text{M}^{-1})</th>
<th>(K_{\text{NMR}}^{\text{eff}}, \text{M}^{-1})</th>
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<tr>
<td>CH(_3)I</td>
<td>I (^b)</td>
<td>10.5±0.9</td>
<td>10.9±0.5</td>
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<tr>
<td></td>
<td>Br(^-)</td>
<td>11.7±1.0</td>
<td>10.7±1.1</td>
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<tr>
<td></td>
<td>Cl(^-)</td>
<td>9.2±0.6</td>
<td>7.0±0.5</td>
</tr>
<tr>
<td></td>
<td>NCS(^-)</td>
<td>2.4±0.5</td>
<td>2.3±0.4</td>
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<tr>
<td></td>
<td>NCO(^-)</td>
<td>9.2±2.1</td>
<td>5.1±0.4</td>
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<td>N(_3)(^-)</td>
<td>10.7±1.3</td>
<td>9.9±0.8</td>
</tr>
<tr>
<td>CHBr(_3)</td>
<td>I (^b)</td>
<td>0.4(^c)</td>
<td>1.0±0.1</td>
</tr>
<tr>
<td></td>
<td>Br(^-)</td>
<td>0.33(^d)</td>
<td>1.4±0.3</td>
</tr>
<tr>
<td></td>
<td>Cl(^-)</td>
<td>-</td>
<td>2.4±0.3</td>
</tr>
<tr>
<td></td>
<td>NCS(^-)</td>
<td>~0.3(^e)</td>
<td>1.2±0.1</td>
</tr>
<tr>
<td></td>
<td>NCO(^-)</td>
<td>~0.1(^e)</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>N(_3)(^-)</td>
<td>~0.4(^e)</td>
<td>-</td>
</tr>
<tr>
<td>CHCl(_3)</td>
<td>I (^b)</td>
<td>-</td>
<td>0.6±0.1</td>
</tr>
<tr>
<td></td>
<td>Br(^-)</td>
<td>-</td>
<td>1.3±0.2</td>
</tr>
<tr>
<td></td>
<td>Cl(^-)</td>
<td>-</td>
<td>1.6±0.2</td>
</tr>
<tr>
<td></td>
<td>NCS(^-)</td>
<td>-</td>
<td>0.5±0.2</td>
</tr>
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\(^a\) In CH\(_3\)CN, calculated (as in earlier studies) assuming that only one type of complex is formed in solutions. \(^b\) Taken as salts with Pr\(_4\)N\(^+\) or Bu\(_4\)N\(^+\) counter-ions. \(^c\) From ref. 51. \(^d\) From ref. 49. \(^e\) From ref. 50.
**Figure S13.** Results of the UV-Vis (A) and $^1$H NMR (B) measurements of solutions with constant concentration of CH$_3$I (5.1 mM) and variable concentrations of Pr$_4$NBr and their simultaneous multivariable fitting to eqs S24 and S25. Note that the combined results of 3 independent series are shown. The table below the figures shows results of the fitting and their statistical analysis which were copied from the output of the fitting (Origin 2016). Figures C and D illustrate *inadequacy* of the fitting assuming that formation of XB do not affect that of HB complexes, and vice versa (i.e., $K_{XB} = C_{XB} / ((C^o_D - C_{XB})(C^o_A - C_{XB}))$ and $K_{HB} = C_{HB} / ((C^o_D - C_{HB})(C^o_A - C_{HB}))$. 

|      | Value     | Standard Error | t-Value | Prob>|t| | Number of Points | Degrees of Freedom | Reduced Chi-Sqr | Residual Sum of Squares | R-Square(COD) | Adj. R-Square |
|------|-----------|----------------|---------|----------------|-----------------|------------------|------------------|-----------------|----------------|---------------|---------------|
| $K_x$| 9.44972   | 0.10228        | 92.38868| 0              | 54              | 51               | 1.31E-04        | 6.68E-03        | 0.99984         | 0.99983       |
| $K_h$| 1.18366   | 0.02208        | 53.59965| 0              |                 |                  |                 |                 |                |               |
| $S_x$| -0.54     | 0              | --      | --             |                 |                  |                 |                 |                |               |
| $S_h$| 2.25      | 0              | --      | --             |                 |                  |                 |                 |                |               |
| $\varepsilon$| 659.9113 | 2.71039        | 243.4748| 0              |                 |                  |                 |                 |                |               |
Results

|       | Value   | Standard Error | t-Value | Prob>|t| |
|-------|---------|----------------|---------|-----|-------|
| Kx    | 10.40763 | 0.14838        | 70.14397| 0   |
| Kh    | 1.9523  | 0.04152        | 47.01999| 0   |
| Sx    | -0.61   | 0              | --      | -- |
| Sh    | 1.91    | 0              | --      | -- |
| $\varepsilon_l$ | 669.05244 | 3.6798        | 181.8178| 0   |

Statistics

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<td>Adj. R-Square</td>
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Figure S14. Results of the UV-Vis (A) and $^1$H NMR (B) measurements of solutions with constant concentration of CH$_3$ (5.1 mM) and variable concentrations of Pr$_4$NCl and their simultaneous multivariable fitting to eqs S24 and S25. (Note, the combined results of 3 independent series). The tables below the figures shows results of the fitting and their statistical analysis which were copied from the output of the fitting (Origin 2016).
Results:

|     | Value | Standard Error | t-Value | Prob>|t| |
|-----|-------|----------------|---------|------|
| Kx  | 1.6953| 0.00607        | 279.2472| 0    |
| Kh  | 0.43096| 0.00287     | 149.982| 0    |
| Sx  | -0.46 | 0              | --      | --   |
| Sh  | 0.98  | 0              | --      | --   |
| εl  | 1028.01652| 2.59311   | 395.6784| 0    |

Statistics

- Number of Points: 40
- Degrees of Freedom: 37
- Reduced Chi-Sqr: 1.25E-06
- Residual Sum of Squares: 4.63E-05
- R-Square(COD): 1
- Adj. R-Square: 0.99999

**Figure S15.** Results of the UV-Vis (A) and 1H NMR (B) measurements of solutions with constant concentration of CHI₃ (5.1 mM) and variable concentrations of Pr₄NNCS and their simultaneous multivariable fitting to eqs S24 and S25. (Note, the combined results of 3 independent series). The tables below the figures shows results of the fitting and their statistical analysis which were copied from the output of the fitting (Origin 2016).
Figure S16. Results of the UV-Vis (A) and $^1$H NMR (B) measurements of solutions with constant concentration of CHI$_3$ (5.1 mM) and variable concentrations of Pr$_4$NN$_3$ and their simultaneous multivariable fitting to eqs S24 and S25. (Note, the combined results of 3 independent series). The tables below the figures shows results of the fitting and their statistical analysis which were copied from the output of the fitting (Origin 2016).
Results

|        | Value  | Standard Error | t-Value  | Prob>|t| | Dependency |
|--------|--------|----------------|----------|-------|-------------|
| Kx     | 0.36855| 0.02599        | 14.18103 | 0     | 0.99964     |
| Kh     | 0.6032 | 0.00707        | 85.29423 | 0     | 0.81803     |
| Sx     | -0.28  | 0              | --       | --    | 0           |
| Sh     | 1.87   | 0              | --       | --    | 0           |
| ε/     | 2580.056 | 169.2578        | 15.24335 | 0     | 0.99963     |

Statistics

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<td>Reduced Chi-Sqr</td>
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**Figure S17.** Results of the UV-Vis (A) and $^1$H NMR (B) measurements of solutions with constant concentration of CHBr$_3$ (5.0 mM) and variable concentrations of Pr$_3$NI and their simultaneous multivariable fitting to eqs S24 and S25. (Note, the combined results of 2 independent series). The tables below the figures shows results of the fitting and their statistical analysis which were copied from the output of the fitting (Origin 2016).
### Results

|       | Value   | Standard Error | t-Value | Prob>|t| |
|-------|---------|----------------|---------|------|
| Kx    | 0.51888 | 0.08104        | 6.40309 | 1.43E-07 |
| Kh    | 0.86927 | 0.02244        | 38.73442| 0    |
| Sx    | -0.31   | 0              | --      | --   |
| Sh    | 2.58    | 0              | --      | --   |
| $\varepsilon_l$ | 1443.278 | 204.2232      | 7.06716 | 1.73E-08 |

### Statistics

- Number of Points: 42
- Degrees of Freedom: 39
- Reduced Chi-Sqr: 7.11E-05
- Residual Sum of Squares: 2.77E-03
- R-Square(COD): 0.99851
- Adj. R-Square: 0.99843

**Figure S18.** Results of the UV-Vis (A) and $^1$H NMR (B) measurements of solutions with constant concentration of CHBr$_3$ (5.0 mM) and variable concentrations of Pr$_4$NBr and their simultaneous multivariable fitting to eqs S24 and S25. (Note, the combined results of 2 independent series). The tables below the figures shows results of the fitting and their statistical analysis which were copied from the output of the fitting (Origin 2016). Br
Results

|    | Value   | Standard Error | t-Value | Prob>|t| | Dependency |
|----|---------|----------------|---------|-------|-----------|
| Kx | 0.09234 | 0.03277        | 2.818   | 0.00755 | 0.99996   |
| Kh | 0.43277 | 0.01081        | 40.04458| 0      | 0.91109   |
| Sx | -0.22   | 0              | --      | --     | --        |
| Sh | 0.99    | 0              | --      | --     | 0         |
| ε/ | 3202.691| 1111.362       | 2.88177 | 0.0064 | 0.99996   |

Statistics

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**Figure S19.** Results of the UV-Vis (A) and 1H NMR (B) measurements of solutions with constant concentration of CHBr₃ (5.0 mM) and variable concentrations of Pr₂NNCS and their simultaneous multivariable fitting to eqs S24 and S25. (Note, the combined results of 2 independent series). The tables below the figures shows results of the fitting and their statistical analysis which were copied from the output of the fitting (Origin 2016).
Comparison of the simultaneous and separate fittings of the UV-Vis and NMR data

Since analysis of the equilibria in the solutions containing CHX$_3$ and anions produced expressions for $\Delta$Abs and $\Delta\delta$ which include K$_{HB}$ and K$_{XB}$ (eqs S24 and S25), we carried out separate fitting of the UV-Vis data measured for each pair using eq S24 and separate fitting of the NMR data using eq S25. Importantly, these fitting were based on the model which takes into account formation of both XB and HB complexes, and produce both K$_{XB}$ and K$_{HB}$ values (in contrast to the earlier studies, in which separate treatments of the UV-Vis and NMR data were done assuming formation of only one type of complex yielding $K_{UV}^{\text{eff}}$ and $K_{NMR}^{\text{eff}}$ values). The principal results of such fitting (K$_{HB}$, K$_{X}$ and their standard errors) are listed in Table S2.

Table S2. Comparison of the results of simultaneous and separate fitting of the UV-Vis and NMR data.

<table>
<thead>
<tr>
<th>Pair</th>
<th>Values from simultaneous (multivariable) fitting</th>
<th>Values from fitting of NMR data only</th>
<th>$K_{(NMR)}/K_{(NMR+UV)}$</th>
<th>Values from fitting of UV-Vis data only</th>
<th>Value</th>
<th>Std Err</th>
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<tr>
<td>CHI$^-$/Br$^-$</td>
<td>K$_{XB}$</td>
<td>9.478</td>
<td>0.103</td>
<td>9.730</td>
<td>0.500</td>
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<td>K$_{HB}$</td>
<td>1.188</td>
<td>0.022</td>
<td>1.229</td>
<td>0.082</td>
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<td>CHI$^-$/T</td>
<td>K$_{XB}$</td>
<td>7.688</td>
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<td>K$_{HB}$</td>
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<td>0.031</td>
<td>1.512</td>
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<td>CHI$^-$/CT</td>
<td>K$_{XB}$</td>
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<td>CHI$^-$/NCS</td>
<td>K$_{XB}$</td>
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<td>K$_{HB}$</td>
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<td>0.003</td>
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<td>CHI$^-$/Ni$^{2+}$</td>
<td>K$_{XB}$</td>
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<td>0.035</td>
<td>1.498</td>
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<tr>
<td>CHBr$_3$/Br$^-$</td>
<td>K$_{XB}$</td>
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<td>K$_{HB}$</td>
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<td>CHBr$_3$/T</td>
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<td>CHBr$_3$/NCS</td>
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<td>0.044</td>
<td>0.087</td>
<td>0.126</td>
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<tr>
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<td>K$_{HB}$</td>
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<td>0.014</td>
<td>0.434</td>
<td>0.040</td>
<td>1.00</td>
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<tr>
<td>Average</td>
<td>0.049 (5.8%)$^a$</td>
<td>0.159 (15.3 %)$^a$</td>
<td>1.16</td>
<td>0.549</td>
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</table>

a) Taking into account formation of both XB and HB complexes. b) Average relative error (i.e. $1/n\Sigma$ (error/value)); c) Ratio of the value obtained from the separate fitting of the NMR data to that obtained from the simultaneous fitting of UV and NMR data.

The K$_{HB}$ and K$_{XB}$ constants resulting from the separate fitting of the NMR data are consistent (within the accuracy of experiments) with the values from the simultaneous fitting of the NMR and UV-Vis data. Yet, the errors from the separate fittings of the NMR data are, on average, about three times higher than that from the simultaneous fitting. Importantly, the calculated shifts of the NMR proton signal depend on the values of $\Delta\delta_{XB}$ and $\Delta\delta_{HB}$ taken from calculation. Since the simultaneous fittings yield the values, which describe variations of UV-Vis spectral data as well, the values resulting from such fitting are apparently more reliable. The values of $\Delta$Abs are related only to the concentration of the XB complexes, and their separate three-parameters fitting using eq S24 produced large standard errors (though the accuracy of the UV-Vis measurements was somewhat higher.
than that of the NMR measurements. Overall, these data indicate that the combine fitting yield more reliable and accurate $K_{HB}$ and $K_{XB}$ values than the separate fittings. Thus, the conclusions of the paper are based on the results of only combined fittings.

It should be also noted that expression for the UV-Vis spectral changes $\Delta \text{Abs} = \varepsilon l \times C_{XB}$ (eq S24 or eq 8 in the text) neglect the spectral changes related to the formation of HB complexes (since spectra of the HB complexes are close to that of the separate molecules). If such changes are taken into account, $\Delta \text{Abs}$ is expressed as:

$$\Delta \text{Abs} = \Delta \varepsilon_{XB} l \times C_{XB} + \Delta \varepsilon_{HB} l \times C_{HB}$$

(S26)

where $\Delta \varepsilon_{XB}$ are $\Delta \varepsilon_{HB}$ differences between extinction coefficients of XB or HB bonded complexes and the separate CHX$_3$ molecules. Eq 26 could be rearranged as:

$$\Delta \text{Abs} = (\Delta \varepsilon_{XB} + \Delta \varepsilon_{HB} C_{HB}/C_{XB}) \times l \times C_{XB}$$

(S27)

Taking into account eq S19, $C_{HB} = K_{HB} C_{XB}/K_{XB}$, leads to

$$\Delta \text{Abs} = (\Delta \varepsilon_{XB} + \Delta \varepsilon_{HB} K_{HB}/K_{XB}) \times l \times C_{XB}$$

(S28)

Accordingly, eqS24 (eq 10 in the text) for fitting of UV-Vis data can be re-written as:

$$\Delta \text{Abs} =$$

$$\varepsilon l \times ((C''A + C''D + 1)/(K_{XB} + K_{HB}) - ((C''A + C''D + 1)/(K_{XB} + K_{HB})) - 4C''A C''D)^{0.5} / (2(1 + K_{HB}/K_{XB}))$$

(S29)

where $\varepsilon = \Delta \varepsilon_{XB} + \Delta \varepsilon_{HB} K_{HB}/K_{XB}$.

Equation S29 is identical to that in eq S24 (or eq 10), but with $\varepsilon = \Delta \varepsilon_{XB} + \Delta \varepsilon_{HB} K_{HB}/K_{XB}$. As such, fitting UV-Vis data using eq 29 would produce the same values of $K_{HB}$ and $K_{XB}$ as that obtained using eq 24. This analysis, however, shows that the extinction coefficients $\varepsilon$ resulted from the separate fitting of UV-Vis data or combined fittings of NMR and UV-Vis data may differ more or less significantly from the extinction coefficients of the halogen-bonded complexes.

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6Somewhat higher accuracy of the UV-Vis measurements is related to two factors, i.e. a) absolute errors in volumes of aliquots used in preparations of the solutions were the same, but the overall volume of the solution used for the UV-Vis measurements were typically twice as higher as that in the NMR; and b) since the ratio of the absolute changes in $\Delta \text{Abs}$ were larger than that of $\Delta \delta$ while the accuracy of the measurements of individual values of Abs and $\delta$ were similar.

The large standard errors in the last column of Table S2 d to two variable parameters ($K_{XB}$, $K_{HB}$) used for $\Delta \delta$ fittings via eq S25. The comparable fittings of the UV-Vis and NMR data (using, in both cases, two variable parameters, $K_{XB}$ and $K_{HB}$, and fixed values of $\varepsilon$ or $\Delta \varepsilon_{XB}$ and $\Delta \varepsilon_{HB}$) yield similar standard errors. For example, the two-parameter fitting of the UV-Vis data for CH$_3$I pair yielded $K_{XB} = 7.660 \pm 0.052$ and $K_{HB} = 1.110 \pm 0.049$, while comparable fitting of the NMR data yielded $K_{XB} = 9.954 \pm 0.423$ and $K_{HB} = 1.512 \pm 0.093$; and fitting of UV-Vis data for CHBr$_3$I pair yielded $K_{XB} = 0.362 \pm 0.002$ and $K_{HB} = 0.604 \pm 0.048$, while NMR data yielded: $K_{XB} = 0.472 \pm 0.058$ and $K_{HB} = 0.630 \pm 0.015$. 
Figure S20. Structures of the [CH$_3$, A$^-$] complexes resulting from the M06-2X/def-TZVPP computations (CH$_3$CN): A$^-$ = Cl$^-$ (A), Br$^-$ (B), I$^-$ (C), N$_3^-$ (D), NCO$^-$ (E), NCS$^-$ (F).
Table S3A. Energies of the XB and HB [CHI₃, A⁻] complexes resulting from the M06-2X/def-TZVPP computations (CH₃CN).*

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<th>BSSE, Hartree</th>
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a) Energies of the separate trihalomethanes CHI₃ -931.58196 CHBr₃ -7761.27261 CHCl₃ -1419.29184 Hartree.
b) ΔE = E_{comp} - (E_{CHX₃} + E_{A}) + BSSE where E_{comp}, E_{CHX₃} and E_{A} are sums of the electronic and ZPE of the complex, CHX₃ and anion and BSSE is a basis set superposition error.
c) HB- or XB- bonded atom of anion (see structures in Figure S19).
Table S3B. Energies of the XB and HB [CHI₃, A⁻] complexes resulting from the M06-2X/def-TZVPP computations (gas phase).²

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a) Energies of the separate trihalomethanes are: CHI₃ -931.57855CHBr₃ -7761.26960CHCl₃ -1419.28913 Hartree. b) ΔE = E_{comp} - (E_{CHX₃} + E_A) + BSSE where E_{comp}, E_{CHX₃} and E_A are sums of the electronic and ZPE of the complex, CHX₃ and anion and BSSE is a basis set superposition error. c) HB- or XB-bonded atom of the anion (see structures in Figure S19).
Table S4. Bond distances and angles in XB and HB complexes.\textsuperscript{ab}

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<th>Angle CH\textsubscript{3}CN</th>
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<td>HB</td>
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\textsuperscript{a) M06-2X/def-TZVPP computations. b) Distances (X...A or H...A), in Å, angles (C-X-A or C-H-A) in deg. c) HB- or XB-bonded atom of the anion (see structures in Figure S19).}
Table S5. Calculated UV and NMR spectral characteristics of XB and HB complexes\textsuperscript{a)}

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<th>Δδ, ppm</th>
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\begin{align*}
Δ &= 0.77\textsuperscript{d} \quad 0.01\textsuperscript{e} \quad -0.05\textsuperscript{f}
\end{align*}

\textsuperscript{a)} From TD DFT and GIAO computations using CH\textsubscript{3}CN-optimized structures. \textsuperscript{b)} Note the calculated values of log ε for the separate CHI\textsubscript{3}, CHBr\textsubscript{3} and CHCl\textsubscript{3} molecules are 3.45, 3.08 and 2.81, respectively. \textsuperscript{c)} Experimental values (Table S1) \textsuperscript{d)} Δ =1/n(Σ (log ε\textsubscript{XB} – log ε\textsubscript{o}) where ε\textsubscript{XB} and ε\textsubscript{o} are extinction coefficients of the XB complex and the separate molecule, respectively. \textsuperscript{e)} Δ =1/n(Σ (log ε\textsubscript{XB} – log ε(exp))). \textsuperscript{f)} Δ =1/n(Σ (log ε\textsubscript{HB} – log ε\textsubscript{o})), where ε\textsubscript{HB} and ε\textsubscript{o} are extinction coefficients of the HB complex and the separate molecule, respectively.
Figure S21. Normalized X…A and H…A separations in the calculated XB or HB complexes (as indicated). \( R_{XA} = d_{XA}/(R_X + R_A) \), where \( d_{XA} \) are H…A or X…A separation, and \( R_X \) and \( R_A \) are van der Waals radii.

Figure S22. Calculated extinction coefficient of the XB and HB complexes CHX₃⁻A⁻ (as indicated). The symbols on the y-axis show values for the separate CHX₃ molecules, for comparison.

Figure S23. Main components of the most intense ground – excited state transition resulted from the TD DFT computations of the XB (left) and HB (right) complexes between CHI₃ and Br⁻.
Atomic coordinates of the XB and HB complexes [CHX₃, A⁻] (M06-2X/def-TZVPP, CH₃CN).

<table>
<thead>
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<th>CH₃-Cl (XB)</th>
<th>CH₃-Cl (HB)</th>
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X-ray Structural Analysis

Co-crystals of CHI\textsubscript{3} with Bu\textsubscript{4}N, Pr\textsubscript{3}NBr or Pr\textsubscript{3}NCI were crystallized by diffusion of hexane into dichloromethane solutions containing 1:1 mixtures of the CHI\textsubscript{3} and alkylammonium salt of halide at low temperatures (-30 °C). Intensity data for X-ray crystallographic analysis were collected at 173 K with a Bruker SMART Apex or Bruker AXS D8 Quest CMOS diffractometer using Mo K\textalpha radiation (\lambda = 0.71073 Å). The structures were solved by direct methods and refined by full matrix least-squares treatment. Intermolecular contacts were analyzed using the OLEX2 structure solution, refinement and analysis program. Crystallographic, data collection and structure refinement details, as well as geometric characteristics of the halogen bonds in these crystals are presented in Table S5. Complete crystallographic data, in CIF format, have been deposited with the Cambridge Crystallographic Data Centre. CCDC 1837582, 1837583 and 1837584 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif.

Table S6. Crystallographic, data collection and structure refinement details

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<tr>
<th>Chemical formula</th>
<th>CHI\textsubscript{3}, Br</th>
<th>CHI\textsubscript{3}, Cl</th>
<th>CHI\textsubscript{3}, I</th>
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<td>615.52</td>
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<tr>
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<td>Monoclinic, Pn</td>
<td>Orthorhombic, Pbca</td>
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<tr>
<td>Temperature (K)</td>
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<td>100</td>
<td>100</td>
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<tr>
<td>a, b, c (Å)</td>
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<td>β (°)</td>
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<td>97.763 (3)</td>
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<tr>
<td>V (Å\textsuperscript{3})</td>
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<td>Mo K\textalpha</td>
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<td>μ (mm\textsuperscript{-1})</td>
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<td>5.00</td>
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<td>Crystal size (mm)</td>
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<tr>
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<td>24409, 3359, 3228</td>
<td>67764, 7607, 6492</td>
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<td>R\textsubscript{int}</td>
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<td>0.080</td>
<td>0.039</td>
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<tr>
<td>(sin θ/λ)\textsubscript{max} (Å\textsuperscript{-1})</td>
<td>0.704</td>
<td>0.602</td>
<td>0.714</td>
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<td>0.035, 0.080, 1.30</td>
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<tr>
<td>No. of reflections</td>
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<td>No. of restraints</td>
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<td>H-atom treatment</td>
<td>H-atom parameters constrained</td>
<td>H-atom parameters constrained</td>
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\(^{1}\text{Diffractometer: Bruker Kappa APEX CCD area detector Absorption correction: Multi-scan SADABS2012/1 (Bruker,2012) was used for absorption correction. wR2(int) was 0.1254 before and 0.0869 after correction. The Ratio of minimum to maximum transmission is 0.5746. The l/2 correction factor is 0.0015. Computer programs: APEX2 V2.1-4 (Bruker, 2007), SAINT V7.23A (Bruker, 2009), Bruker SAINT, SHELXT (Sheldrick, 2008), SHELXL (Sheldrick, 2008), Olex2 (Dolomanov et al., 2009).}^{2}\text{Diffractometer: Bruker Kappa APEX CCD area detector Absorption correction: Multi-scan SADABS2012/1 (Bruker,2012) was used for absorption correction. wR2(int) was 0.1182 before and 0.0970 after correction. The Ratio of minimum to maximum transmission is 0.8552. The l/2 correction factor is 0.0015.}^{3}\text{Diffractometer: Bruker AXS D8 Quest CMOS diffractometer. Absorption correction: Multi-scan SADABS 2016/2: Krause, L., Herbst-Iimer, R., Sheldrick G.M. & Stalke D., J. Appl. Cryst. 48 (2015) 3-10. Computer programs: Apex3 v2016.9-0 (Bruker, 2016), SAINT V8.37A (Bruker, 2016), SHELXS97 (Sheldrick, 2008), SHELXL2016/6 (Sheldrick, 2015, 2016), SHELXLE Rev714 (Hübschle et al., 2011).}
Figure S24. Halogen-bonded networks in the co-crystals of CHI₃ with Pr₄NCl (top), Pr₄NBr (middle) and Bu₄NI (bottom).

Table S7. Bond distances (I…X, in Å) and angles (C-I-A, in deg) in the halogen-bonded complexes in the solid-state structures in comparison with the calculated structures.

<table>
<thead>
<tr>
<th>A'</th>
<th>X-ray crystallographic measurements</th>
<th>M06-2X/def-TZVPP computations (CH₃CN)</th>
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<td>∠C-I-A, deg&lt;sup&gt;a&lt;/sup&gt;</td>
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<td>170.21, 173.14, 166.29</td>
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<tr>
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<td>170.6, 168.46, 177.92</td>
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<td>Cl&lt;sup&gt;−&lt;/sup&gt;</td>
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