Strength of the [Z–I···Hal]$^-$ and [Z–Hal···I]$^-$ halogen bonds: electron density properties and halogen bond length as estimators of interaction energy

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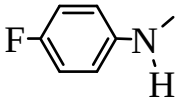
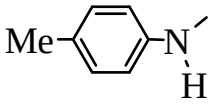
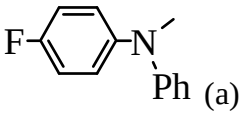
Supplementary Material

Table S1. Relationships between interaction energy (E_{int}, kcal/mol) and electron density based estimators.

Type of interaction	Estimator	Relationship	Reference
H…O	V_b	$E_{int} \sim 0.5V_b$	[81]
FH…FR	G_b	$E_{int} \sim -0.429G_b$	[82,85]
	V_b	$E_{int} \sim 0.37V_b - 3.1$	[82]
	ρ_b	$E_{int} \sim -186\rho_b + 2.3$	[82]
	$\nabla^2\rho_b$	$E_{int} \sim -2.52\nabla^2\rho_b - 5.2$	[82]
	$\lambda_{\parallel,b}$	$E_{int} \sim -6.7\lambda_{\parallel,b} + 2.3$	[82]
Cl…X[b]	V_b	$E_{int} \sim 0.49V_b$	[118]
	G_b	$E_{int} \sim -0.47G_b$	[118]
Br…X[b]	V_b	$E_{int} \sim 0.58V_b$	[118]
	V_b	$E_{int} \sim 0.375V_b - 0.57$	[119]
	G_b	$E_{int} \sim -0.57G_b$	[118]
I…X[b]	V_b	$E_{int} \sim 0.68V_b$	[118]
	V_b	$E_{int} \sim 0.556V_b + 0.64$	[119]
	G_b	$E_{int} \sim -0.67G_b$	[118]
F···F	G_b	$E_{int} \sim -0.129G_b$	[86]
Cl…Cl	V_b	$E_{int} \sim -0.1006V_b^2 - 0.218V_b - 0.55$	[116]
	G_b	$E_{int} \sim -0.0841G_b^2 + 0.367G_b - 0.84$	[116]
	ρ_b	$E_{int} \sim -535.9\rho_b^2 + 31.13\rho_b - 0.87$	[116]
	$\nabla^2\rho_b$	$E_{int} \sim -0.09e^{2.405\nabla^2\rho_b} - 0.17$	[116]
	$\lambda_{\parallel,b}$	$E_{int} \sim -0.099e^{1.762\lambda_{\parallel,b}} - 0.17$	[116]
Br…Br	V_b	$E_{int} \sim -0.0926V_b^2 - 0.173V_b - 0.16$	[116]
	G_b	$E_{int} \sim -0.1178G_b^2 + 0.73G_b - 1.5$	[116]
	ρ_b	$E_{int} \sim -380.6\rho_b^2 + 24.78\rho_b - 0.42$	[116]
	$\nabla^2\rho_b$	$E_{int} \sim -0.07e^{2.624\nabla^2\rho_b} + 0.1$	[116]
	$\lambda_{\parallel,b}$	$E_{int} \sim -0.3e^{1.306\lambda_{\parallel,b}} + 0.71$	[116]
I…I	V_b	$E_{int} \sim -0.0635V_b^2 - 0.217V_b - 0.25$	[116]
	G_b	$E_{int} \sim -0.1564G_b^2 + 1.138G_b - 2.25$	[116]
	H_b	$E_{int} \sim 2.35H_b - 1.87$	[116]
	ρ_b	$E_{int} \sim -305.2\rho_b^2 + 21.78\rho_b - 0.44$	[116]
	$\lambda_{\parallel,b}$	$E_{int} \sim -0.031e^{2.818\lambda_{\parallel,b}} + 0.25$	[116]

[a] V_b, G_b, and H_b in kcal/(mol•bohr^3), ρ_b in e/Å^3, $\nabla^2\rho_b$ and $\lambda_{\parallel,b}$ in e/Å^5. [b] X = N, S, O, C in ref. [118], X = O, N, F in ref. [119].

Table S2. Calculated structures.

<table>
<tr><th colspan="4">[(A)_nZ–Y•••X][–] (Y = I, X = F, Cl, Br, I; Y = Cl, Br, X = I)</th></tr>
<tr>
<td>
Z = Hal
(A)_nZ = F
Cl, Br
I
</td>
<td>
Z = N
(A)_nZ = H₂N–
Me₂N–
H(Ph)N–
Ph₂N– (a)
 
 
 
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 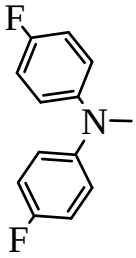
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 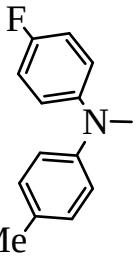
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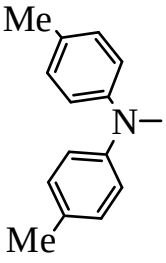
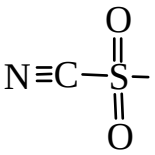
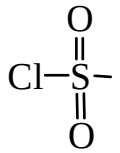
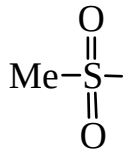
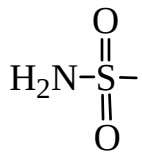
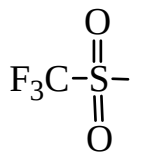
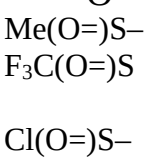
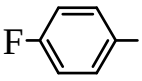
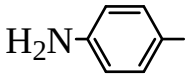
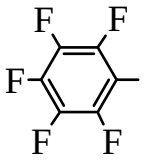
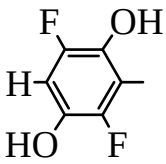
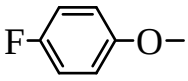
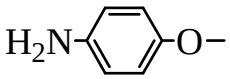
 
(a)
</td>
<td>
Z = N
(A)_nZ = C=N–
H₂C=N–
F₂C=N–
Me₂C=N–
O₂N–
</td>
<td>
Z = P
(A)_nZ = H₂P–
H(F)P–
F₂P–
Cl₂(O=)P–
F₂(O=)P–
H₂(O=)P–
H(F)(O=)P–
Me₂(O=)P–
</td>
</tr>
<tr>
<td>
Z = C (sp³)
(A)_nZ = Me
H₂(Me)C–
H(Me)₂C–
Me₃C–
H₂FC–
H(F)₂C–
F₃C–
</td>
<td rowspan="2">
Z = S
(A)_nZ =
 
N≡C–S(=O)(=O)–
 
Cl–S(=O)(=O)–
 
Me–S(=O)(=O)–
 
H₂N–S(=O)(=O)–
 
F₃C–S(=O)(=O)–
 
Me(O=)S–
F₃C(O=)S
–
Cl(O=)S–
N≡C(O=)S
–
</td>
<td>
Z = B
(A)_nZ = F₂B–
H₂B–
H(F)B–
H(HO)B–
</td>
</tr>
<tr>
<td>
Z = C (sp²)
(A)_nZ = H₂C=CH–
H(O=)C–
Me(O=)C–
(MeO)(O=)C–
Ph
 
 
 
 
(a)
</td>
<td>
Z = Si
(A)_nZ = Me₃Si–
F₃Si–
H3Si–
H₂(F)Si–
H(F)₂Si–
</td>
</tr>
<tr>
<td>
Z = C (sp²)
(A)_nZ = HC≡C–
MeC≡C–
FC≡C–
</td>
<td></td>
<td>
Z = O
(A)_nZ = HO–
MeO–
PhO–
 
 
Z = H
(A)_nZ = H
</td>
</tr>
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(a) Except Y = X = I.

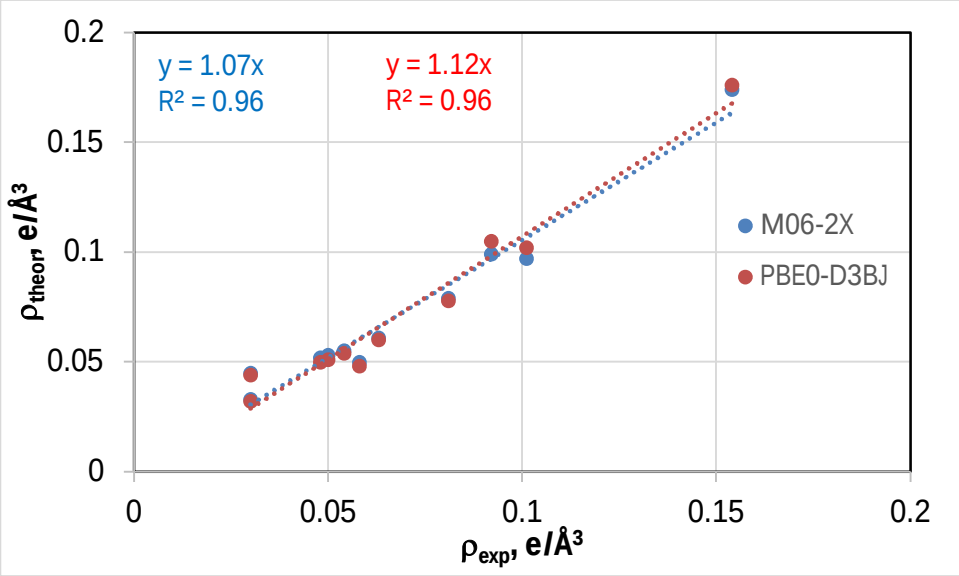

Figure S1. Correlations between theoretical and experimental values of the electron density (see Table 3 for details).

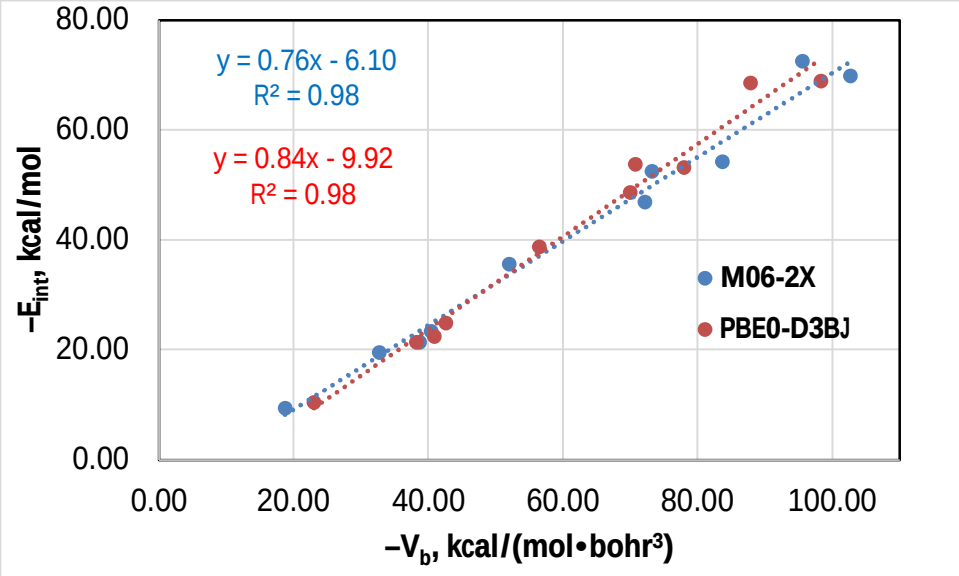

Figure S2. Correlations between $-E_{int}$ and $-V_b$ calculated at the M06-2X/ADZP-DKH and PBE0-D3BJ/ADZP-DKH levels of theory.

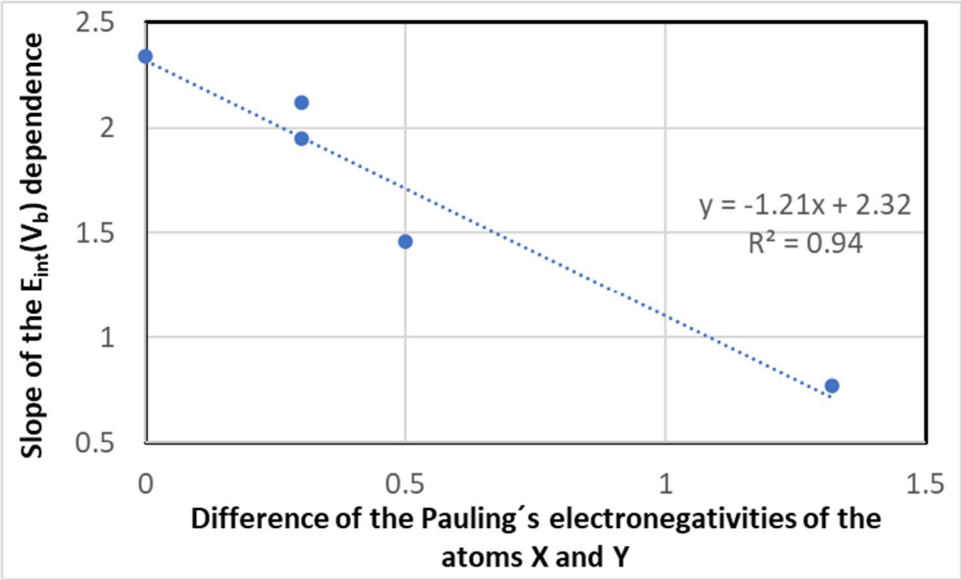

Figure S3. Plot of the slope of the $E_{int}(V_b)$ dependence against difference of the Pauling´s electronegativities of the atoms X and Y in structures $[(A)_nZ–I\cdots X]^-$ and $[(A)_nZ–Br\cdots I]^-$ (X = F, Cl, Br, I).

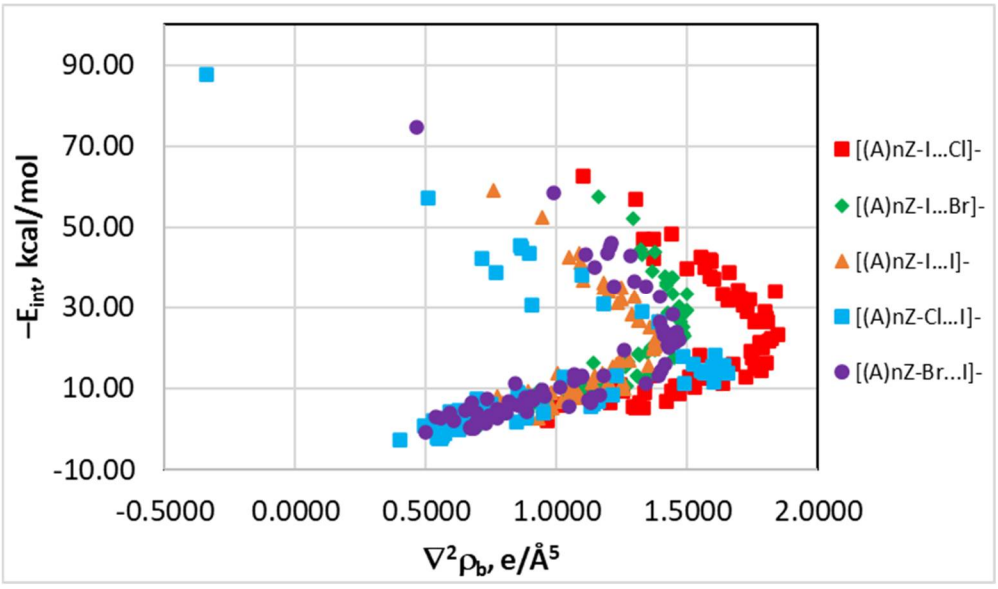

Figure S4. Plots of $-E_{int}$ *vs.* $\nabla^2\rho_b$.

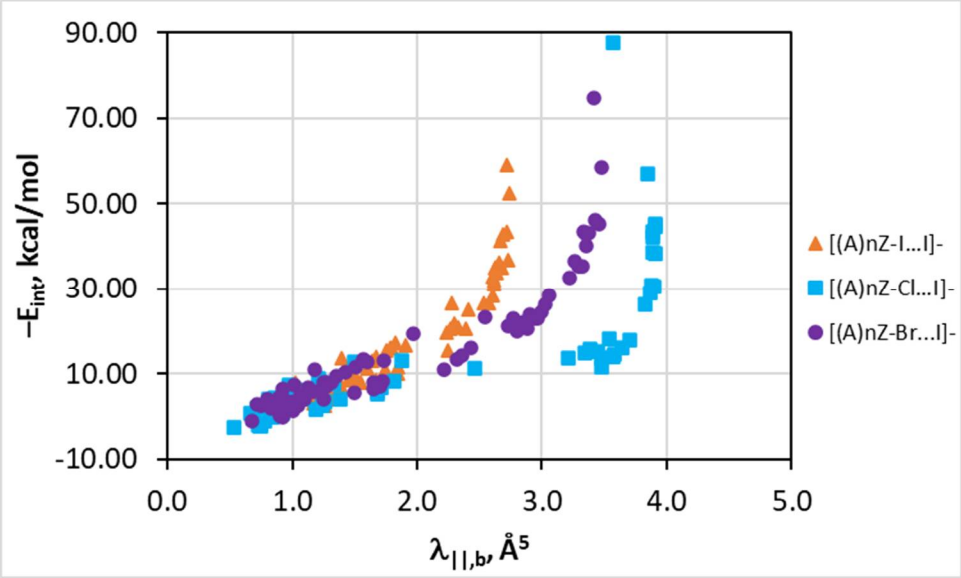

Figure S5. Plots of $-E_{int}$ *vs.* $\lambda_{||,b}$.

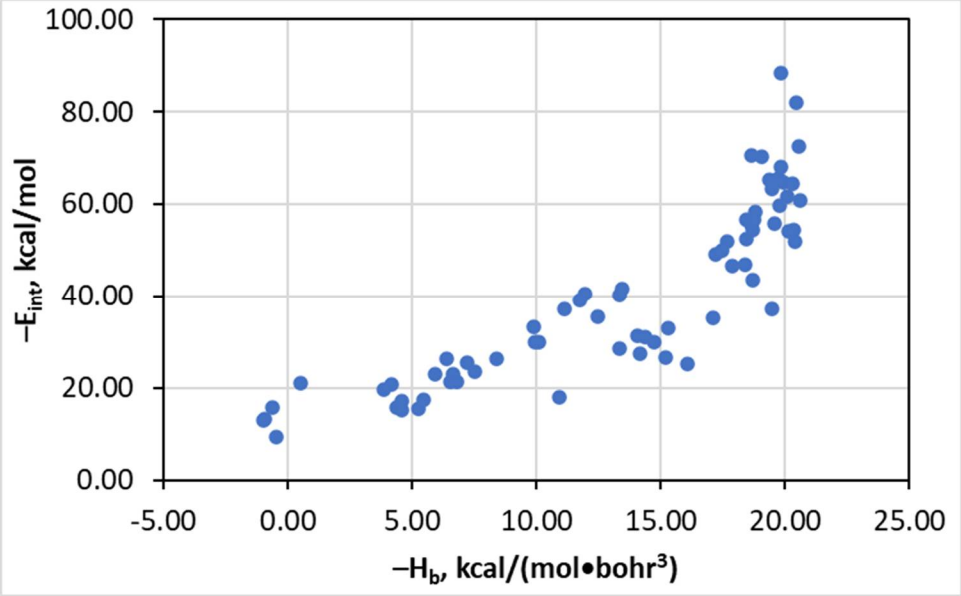

Figure S6. Plot of $-E_{int}$ *vs.* $-H_b$ for the $[(A)_nZ–I•••F]^-$ series.

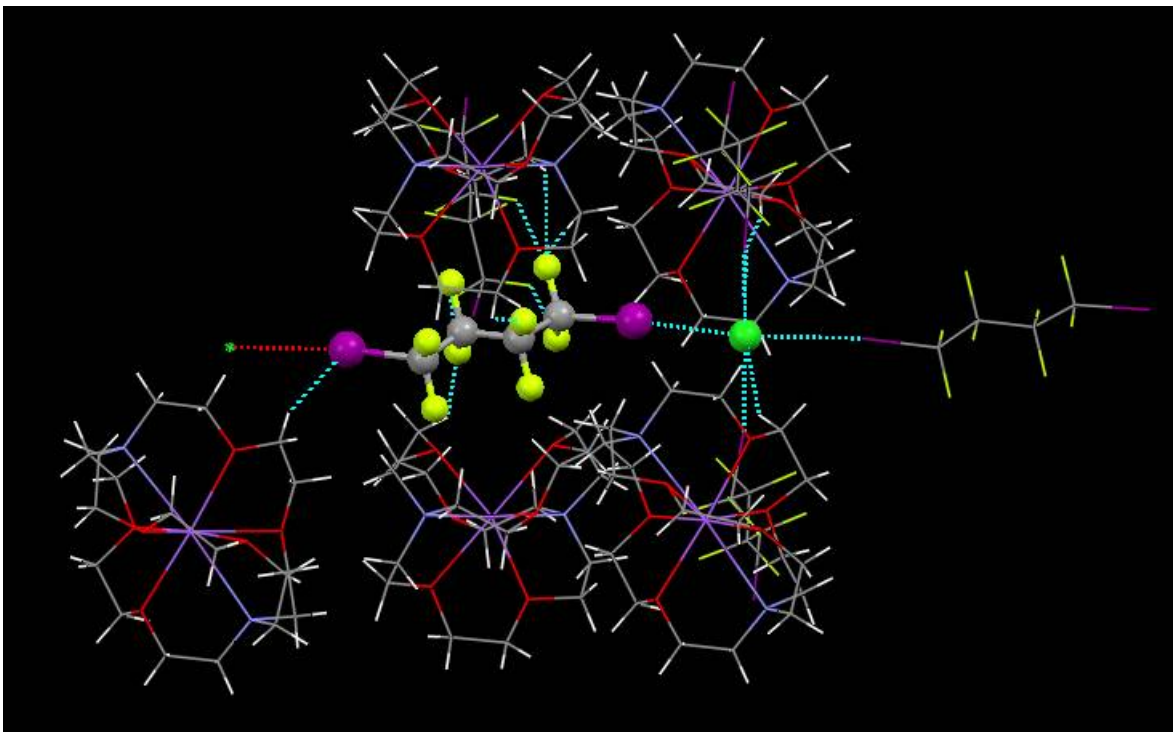

Figure S7. Example of the adequate cluster for the direct estimates of E_{int} between the fragments I–C_4F_8–I and Cl^- in the X-ray structure ACIPOU.

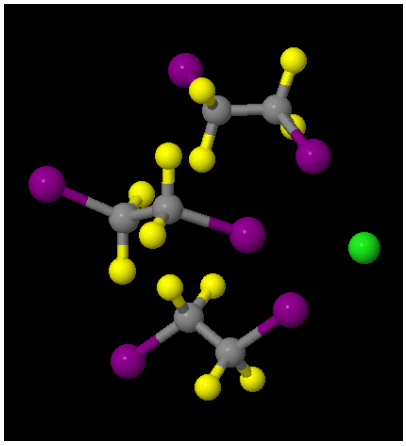

Figure S8. Four-molecule computational model of the structure ACIPIO (criterium for this model was inclusion of all ICF_2CF_2I fragments with the nearest neighbor I•••Cl distance in the three directions of 3.73 Å relatively to the given Cl^- ion. E_{int} for the individual I•••Cl contact was calculated as $E_{int}(I•••Cl) = E_{int}(total)/3$, where $E_{int}(total)$ is the total interaction energy between $(ICF_2CF_2I)_3$ and Cl^-).