

Supplementary Materials

Astatine facing Janus: halogen bonding vs. charge-shift bonding

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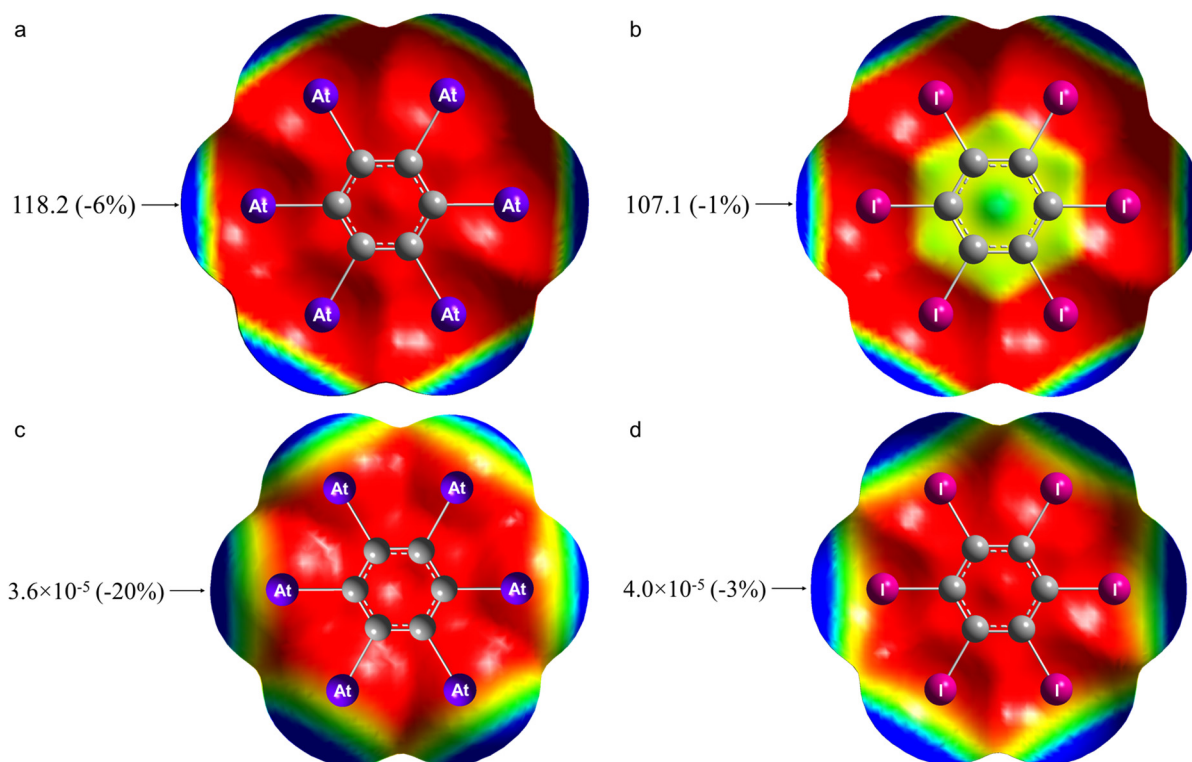


Figure S1. 2c-PW6B95D3/TZVPPD calculated electrostatic potential (a, b) and local electrophilicity (c, d) at the C_6At_6 and C_6I_6 molecular surfaces (defined by 0.001 a.u. density isosurfaces). The maximum values, $V_{S,max}$ and $\omega_{S,max}^+$, at the astatine and iodine σ -holes are in $\text{kJ}\cdot\text{mol}^{-1}$ and a.u., respectively. Values in parenthesis represent the SOC effects. Color code: from red (lowest values) to blue (highest values).

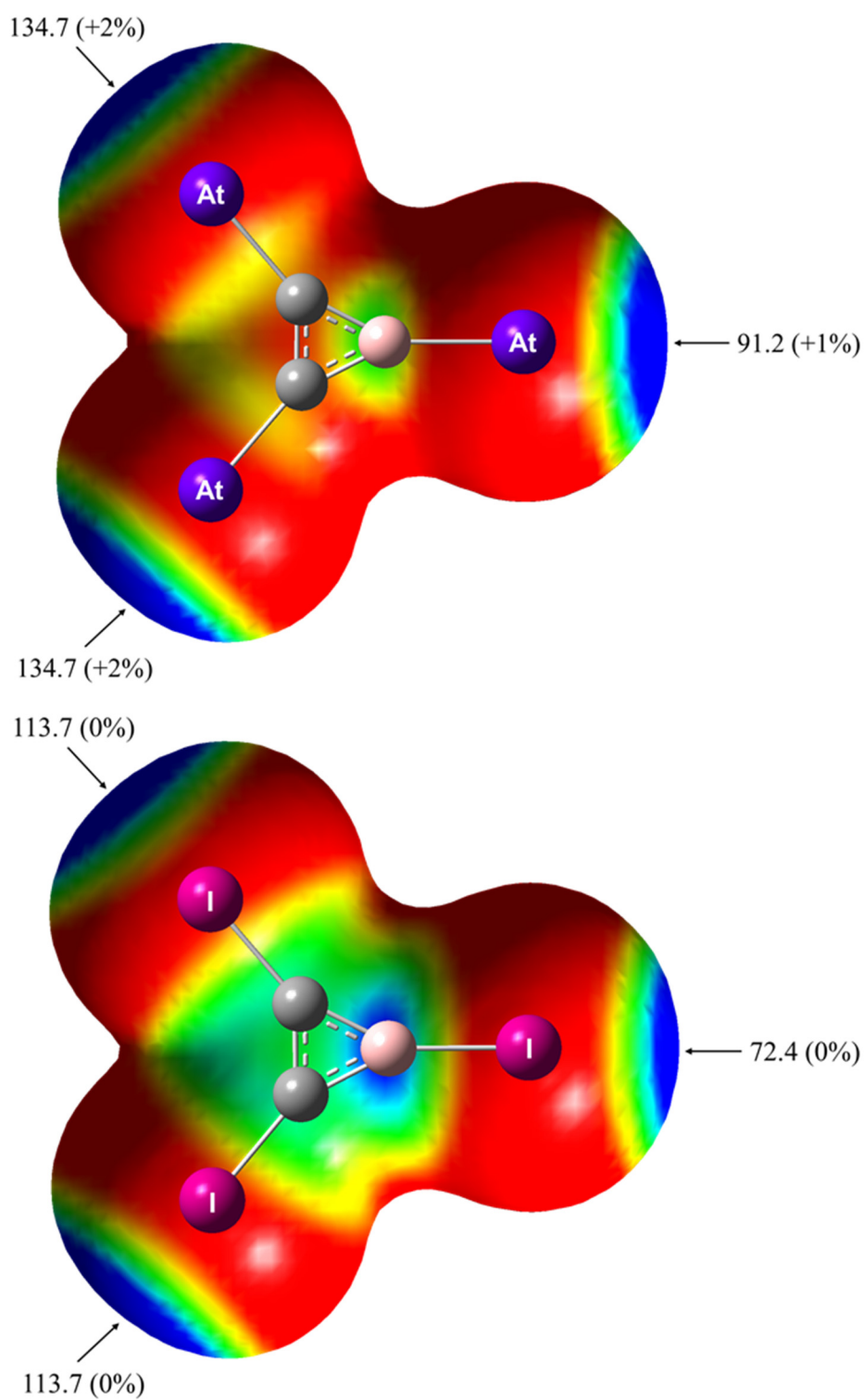


Figure S2. $2c$ -PW6B95D3/TZVPPD calculated electrostatic potential at the C_2BI_3 and C_2BI_3 molecular surfaces (defined by 0.001 a.u. density isosurfaces). The maximum values, $V_{S,max}$, at the astatine and iodine σ -holes are in $\text{kJ}\cdot\text{mol}^{-1}$ (SOC effects are given in parenthesis). Color code: from red (most negative values) to blue (most positive values).

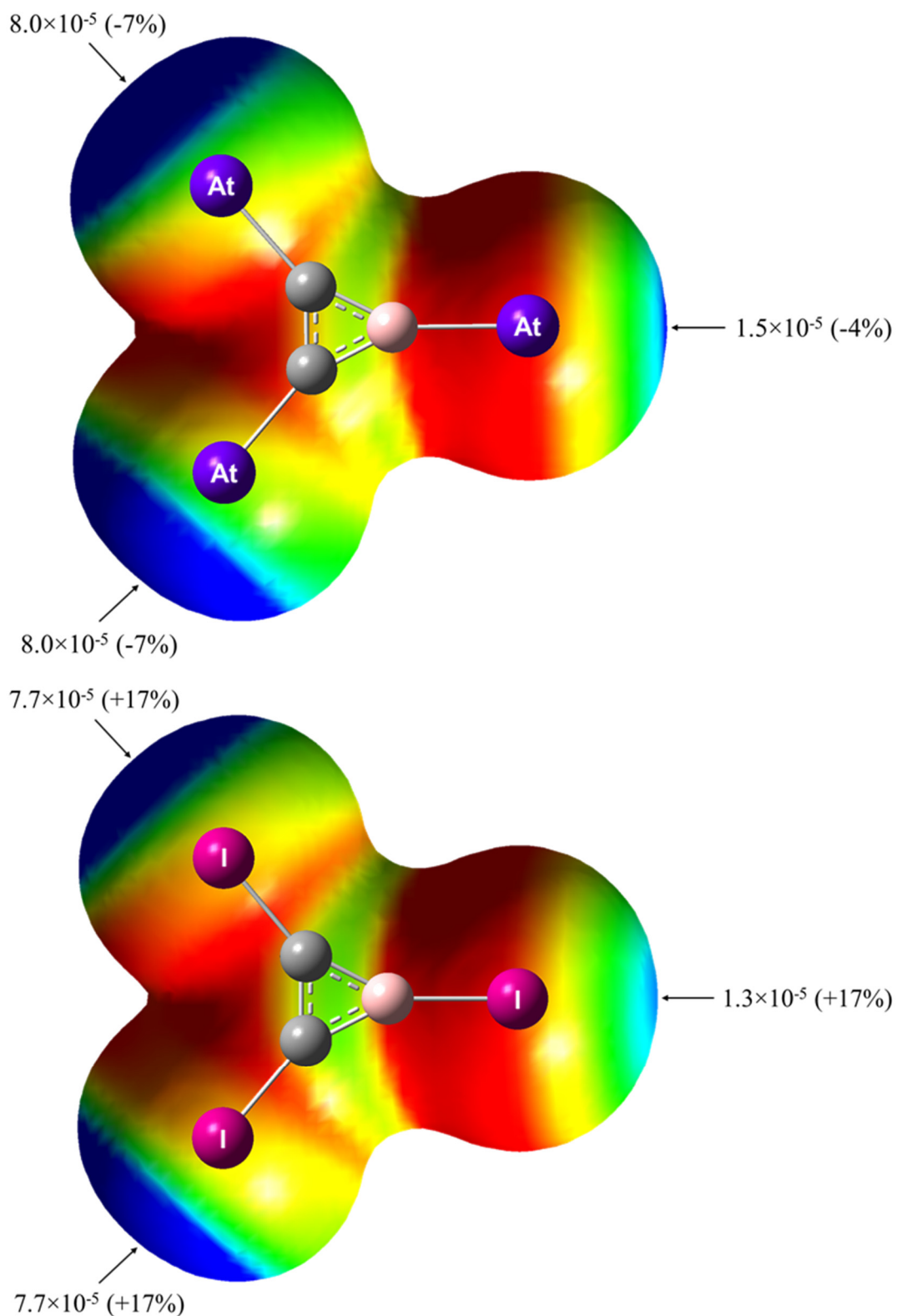


Figure S3. Local electrophilicity, at the C_2BI_3 and C_2BAI_3 molecular surfaces (defined by the 0.001 a.u. density isosurface) calculated at the 2c-PW6B95D3/TZVPPD level of theory. The most positive electrophilicity values, $\omega^+_{S,max}$, at the astatine and iodine σ -holes are in a.u. Values in parenthesis represent SOC effects are given in parenthesis. Color code: from red (lowest values) to blue (highest values).

Table S1. Selected QTAIM descriptors (in a.u.) obtained at the 2c-PW6B95-D3/TZVPPD level of theory for C–C bonds in C₆X₆ species (X = I, At).

	ρ_b^b	$\nabla^2\rho_b^c$	$ V_b /G_b^d$	$\delta(C, C)^e$	FLU ^f
X = I	0.31	-0.90	4.05	1.35	0.0057
ΔSO^a	+0.00	-0.02	+0.02	+0.00	-0.0005
X = At	0.32	-0.92	3.96	1.38	0.0004
ΔSO^a	+0.01	-0.05	-0.03	+0.02	-0.0033

^a Defined as the difference between the results of 2c-PW6B95-D3/TZVPPD and sr-PW6B95-D3/TZVPPD calculations. ^b Electron density at the BCP. ^c Laplacian of the electron density at the BCP. ^d Ratio between the potential energy density and the (positive definite) kinetic energy density at the BCP. ^e Delocalization index. ^f Aromaticity index $FLU = \sum_1^n \left(\frac{\delta(C, C) - \delta_{ref}(C, C)}{\delta_{ref}(C, C)} \right)^2$ with n equal to the number of members in the ring, and $\delta_{ref}(C, C) = 1.388$ according to PW6B95-D3/TZVPPD calculations on the benzene molecule. Low values indicate a strong aromaticity character.

Table S2. Interaction distances, lengthening of C–X bonds upon complexation, interaction angles and directionality angles for the C₆X₆⋯C₆Y₆ complexes (X, Y = I, At) at the counterpoise-corrected sr-MP2/TZVPPD level of theory.

	X = I, Y = At		X = At, Y = I	
	I⋯C	I⋯At	At⋯C	At⋯I
$d_{X\dots C}$ (Å)	3.373	-	3.400	-
$d_{X\dots Y}$ (Å)	-	3.903	-	3.784
Δd_{C-X} (Å)	0.005	0.005	0.007	0.007
α_{CXC} (°)	164.8	160.0	162.5	159.4
α_{XYC} (°)	109.4	68.2	103.4	72.7

Table S3. Scalar relativistic PW6B95-D3/TZVPPD and MP2/TZVPPD counterpoise corrected interaction energies and related parameters: interaction distances, lengthening of R–X bonds upon complexation (R = B, C), and interaction angles, for the C₂BX₃⋯C₂BY₃ complexes (X, Y = I, At).

	ΔE^{CP} (kJ/mol)	$d_{\text{X}\dots\text{N}}$ (Å)	$\Delta d_{\text{C-X}}$ (Å)	α_{CXN} (°)	
sr-PW6B95-D3	I _B –XB	-13.3	3.711	0.000	172.3
	I _C –XB	-14.9	3.597	0.000	178.1
	At _B –XB	-13.8	3.712	0.001	173.1
	At _C –XB	-15.4	3.587	0.001	175.5
sr-MP2	I _B –XB	-14.3	3.610 ^a	0.001 ^a	173.0 ^a
	I _C –XB	-16.5	3.481 ^a	0.002 ^a	177.5 ^a
	At _B –XB	-14.4	3.622 ^a	0.003 ^a	173.1 ^a
	At _C –XB	-16.5	3.485 ^a	0.003 ^a	177.2 ^a

^a Counterpoise-corrected values.