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Electronic supplementary information

Size-dependent conformational change in halogen- π interaction: from benzene to graphene

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I. Computational Details

The geometries of the two distinct low energy conformers were determined in a prescreening of possible conformations using relatively low computational cost dispersion-corrected DFT (DFT-D3) geometry optimizations followed by the resolution of identity (RI). Specifically, the X₂-Benzen (Bz) T-shaped structure showed X₂ molecules located on top of the center of carbon bond and other T-shaped structure showed X₂ molecules located on top of the carbon atom. In the next step, overall calculations of aromatic compounds (benzene, naphthalene, pyrene, coronene, and graphene) were performed using hybrid functional PBE0 with the dispersion-corrected D3 method, Tkatchenko-Scheffler dispersion correction scheme, and the aug-cc-pV*NZ*(aV*NZ*, *N*=D,T,Q) basis set. The geometries for the Gaussian basis set, tier basis set, and plane wave basis set were optimized at the aVQZ level of theory (except for the X₂-coronene (Cor) case on the PBE0-D3/aVDZ geometry), the light-tier 2 and light-tier 3 levels, and the 500-eV energy cut-off level, respectively. The binding energy of each conformer for the Gaussian basis set was obtained from the basis set superposition error (BSSE)-corrected value. The complete basis set (CBS) limit binding energies at the DFT/CBS level were obtained with the least biased pseudo-interpolation scheme which connects the BSSE-corrected (E^b) and BSSE-uncorrected (E^u) energies at 1/N=0 (i.e.,N= ∞). These asymptotic values are calculated by the equation

$$E_{CBS*} = (\delta_N \varepsilon_{N+1} - \delta_{N+1} \varepsilon_N) / (\delta_N - \delta_{N+1}),$$

where $\varepsilon_N [= (E^b_N + E^u_N)/2]$ is the median value of E^b and E^u and $\delta_N [= (E^b_N - E^u_N)]$ is the BSSE.

Fritz Haber Institute *ab initio* molecular simulations (FHI-AIMS) package¹ was used for TS dispersion corrections. The DFT-D3 calculations were done using Turbomole² and NBO charge and EPM was obtained using Gaussian09,³ while CCSD(T) calculations and DFT symmetry adapted perturbation theory (SAPT) analysis were carried out using Molpro.⁴ The optimized geometries were drawn using the Gaussview5.0 and Posmol⁵ packages.



Figure S1. Two distinct conformers of small π -system used in DFT-SAPT calculation optimized at the PBE0-D3/aug-cc-pVTZ level.

Table S1. Binding energies (ΔE in kJ/mol) and vertical distances (d_v in Å, in italic, in parentheses) of T-shaped and Stacked structures of Cl₂/Br₂ on benzene, naphthalene, pyrene, coronene and graphene (See Table 1 in text for higher level calculation results).

Conformer	PBE-D3 /CBS	PBE-D3 /500eV	PBE0-TS /light-tier3*	(light-tier3)		
Cl ₂ /Br ₂ -Benzene						
T-Shaped	16.43/20.90	16.92/22.68	11.01/15.27	(3.29/3.08)		
Stacked	8.57/9.73	8.65/9.71	8.78/9.69	(3.58/3.70)		
Cl ₂ /Br ₂ -Naphthalene						
T-Shaped	15.18/18.85	15.42/19.83	12.35/15.55	(3.19/3.27)		
Stacked	11.56/13.01	11.48/13.03	12.24/13.53	(3.72/3.80)		
Cl ₂ /Br ₂ -Pyrene						
T-Shaped	17.17/21.09	17.21/21.84	13.96/17.45	(3.16/3.22)		
Stacked	14.78/17.14	14.79/17.28	15.58/17.48	(3.62/3.69)		
Cl ₂ /Br ₂ -Coronene				(light-tier2)		
T-Shaped	17.79/22.19	18.08/22.88	15.06/18.86	(3.07/3.19)		
Stacked	16.78/20.49	16.60/19.94	17.70/20.31	(3.48/3.61)		
Cl ₂ /Br ₂ -Graphene				(light-tier2)		
T-Shaped		20.45/25.59	16.86/20.44	(3.16/3.14)		
Stacked		22.20/30.87	21.74/25.71	(3.42/3.56)		

*PBE0-TS binding energies of graphene are obtained using the light-tier2 basis set.

II. NBO Charges of π systems















Figure S2. NBO charges of carbon atoms of each aromatic systems (C_6H_6 , $C_{10}H_8$, $C_{16}H_{10}$, $C_{24}H_{12}$, $C_{54}H_{18}$, $C_{96}H_{24}$, and $C_{150}H_{30}$).



Figure S3. Labelling of circumference carbon layer (R_n) used in Figure 2.

III. QTAIM analysis of the X_2 - π systems.

The quantum theory of atoms in molecules (QTAIM) analysis⁶ was performed to determine the presence of bond critical points ((3,-1) BCPs) of intermolecular halogen bonding interactions in aromatic π -system····Cl₂. The IUPAC defines halogen bond as "R-X····Y-Z occurs when there is evidence of a net attractive interaction between an electrophilic region on a halogen atom X belonging to a molecule or a molecular fragment R-X (where R can be another atom, including X, or a group of atoms) and a nucleophilic region of a molecule, or a molecular fragment Y-Z".⁷ To study halogen bonds, investigating the properties of bond critical point between two fragments would be one of the prevalent methods. The following CP descriptors were considered: the electron density value, $\rho(r)$; density Laplacian value, $\nabla^2 \rho(r)$; energy density H(r); and the $\frac{-G(r)}{V(r)}$ ratio.

Laplacian of the electron density corresponds to the local curvature of ρ (r) and indicates whether the electron density is depleted, $\nabla^2 \rho$ (r) > 0, or locally concentrated, $\nabla^2 \rho$ (r) < 0 at a given point in space. Moreover, Laplacian is related to the local components, kinetic and potential, of the interaction energy by a local expression of the virial theorem (in a.u.):^{8,9}

$$\frac{\hbar}{4m}\nabla^2\rho(r) = 2\ G(r) + V(r)$$

where G(r) is the electronic kinetic energy density and V(r) is the electronic potential energy density. The ratio $\frac{-G(r)}{V(r)}$ was used before for characterization of halogen bonds,¹⁰ that if $\frac{-G(r)}{V(r)} > 1$ and H (r) is a small, positive number, the interaction is classified as "closed-shell". Accordingly, halogen bonds can be topologically classified if the following parameters are satisfied: low value of ρ (r), positive sign of $\nabla^2 \rho$ (r), low value of H (r), and $\frac{-G(r)}{V(r)} > 1$. All QTAIM calculations were performed with MultiWfn package¹¹ with .fchk files generated in Gaussian used as the input.

Complex	ρ (r)	$\nabla^2 \rho$ (r)	H(r)	-G(r)/V(r)
Bz-T-shaped	0.0116	0.0363	0.00192	1.37

Table S2. Topological parameters (in atomic units) for X...D (3,-1) critical points

0.0038

0.0036

0.0095

N.A.

Bz-Stacked

Cor-T

Ex-Cor-Stacked

Based on Figure S4, T-shaped conformer of benzene forms a halogen bond, in accordance to IUPAC definition of halogen bonding. The critical point present in the Stacked conformer of Bz-Cl₂ cannot be accounted for halogen bond due to its nonlinearity. As discussed in the main text, the Stacked conformer is more favored for extended aromatic systems. T-shaped conformer for coronene

0.0114

0.0100

0.0302

N.A.

0.00041

0.00039

0.00138

N.A.

1.21

1.23

1.29

N.A

still exhibits halogen bonding; however, this does have competing energy with the Stacked conformer. As seen in figure below, there is no longer a critical point between the halogen and π -system of the Stacked conformer of extended coronene. This guarantees that halogen bonding is no longer a major contributing noncovalent interaction for much more extended aromatic systems such as graphene.



Figure S4. Molecular graphs of complexes analyzed in this study; big circles correspond to attractors (C: yellow; H: white; Cl: green), small ones to critical points (orange: bond critical point ((3, -1) BCP); yellow: ring critical point ((3, +1) RCP); green: cage critical point ((3, +3) CCP)).

IV. Anisotropic hard wall distance



Figure S5. Anisotropic hard wall distance (Å) of a halogen atom in diatomic halogen molecules (Cl_2 and Br_2) for two different orientations (0° and 90°): Cl (3.00 and 3.33), Br (3.08 and 3.47) at the CCSD(T)/CBS level. The corresponding van der Waals distances are Cl (3.35 and 3.72), Br (3.44 and 3.88).

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