Supplementary Information

Dynamic and Static Behavior of the H---π and E---π Interactions in EH_2 Adducts of Benzene π-System (E = O, S, Se and Te), Elucidated by QTAIM Dual Functional Analysis

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QTAIM Dual Functional Analysis (QTAIM-DFA)

The bond critical point (BCP; ∗) is an important concept in QTAIM. The BCP of $(\omega, \sigma) = (3, -1)$[S1] is a point along the bond path (BP) at the interatomic surface, where charge density $\rho(\boldsymbol{r})$ reaches a minimum. It is donated by $\rho_b(\boldsymbol{r}_c)$. While the chemical bonds or interactions between A and B are denoted by A–B, which correspond to BPs between A and B in QTAIM, A-∗-B emphasizes the presence of BCP (∗) in A–B.

The sign of the Laplacian $\rho_b(\boldsymbol{r}_c)$ ($\nabla^2\rho_b(\boldsymbol{r}_c)$) indicates that $\rho_b(\boldsymbol{r}_c)$ is depleted or concentrated with respect to its surrounding, since $\nabla^2\rho_b(\boldsymbol{r}_c)$ is the second derivative of $\rho_b(\boldsymbol{r}_c)$. $\rho_b(\boldsymbol{r}_c)$ is locally depleted relative to the average distribution around $\boldsymbol{r}_c$ if $\nabla^2\rho_b(\boldsymbol{r}_c) > 0$, but it is concentrated when $\nabla^2\rho_b(\boldsymbol{r}_c) < 0$. Total electron energy densities at BCPs ($H_b(\boldsymbol{r}_c)$) must be a more appropriate measure for weak interactions on the energy basis.[S1-S6] $H_b(\boldsymbol{r}_c)$ are the sum of kinetic energy densities ($G_b(\boldsymbol{r}_c)$) and potential energy densities ($V_b(\boldsymbol{r}_c)$) at BCPs, as shown in eqn (S1). Electrons at BCPs are stabilized when $H_b(\boldsymbol{r}_c) < 0$, therefore, interactions exhibit the covalent nature in this region, whereas they exhibit no covalency if $H_b(\boldsymbol{r}_c) > 0$, due to the destabilization of electrons at BCPs under the conditions.[S1] Eqn (S2) represents the relation between $\nabla^2\rho_b(\boldsymbol{r}_c)$ and $H_b(\boldsymbol{r}_c)$, together with $G_b(\boldsymbol{r}_c)$ and $V_b(\boldsymbol{r}_c)$, which is closely related to the virial theorem.

$$H_b(\boldsymbol{r}_c) = G_b(\boldsymbol{r}_c) + V_b(\boldsymbol{r}_c) \quad \text{(S1)}$$

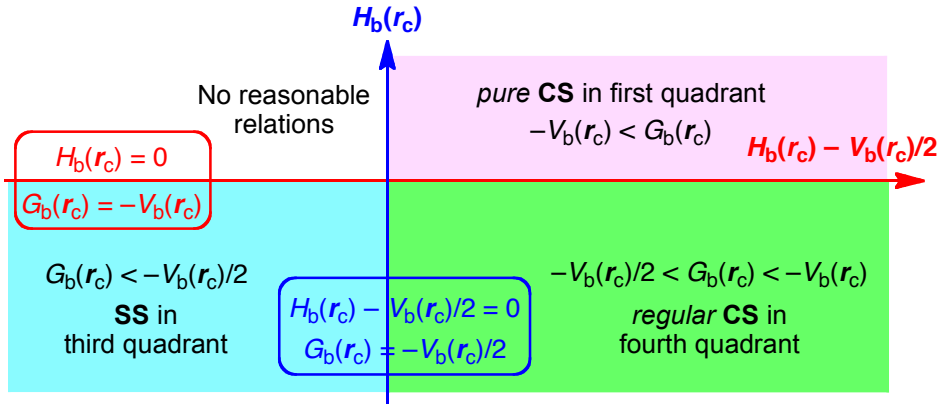
$$(\hbar^2/8m)\nabla^2\rho_b(\boldsymbol{r}_c) = H_b(\boldsymbol{r}_c) - V_b(\boldsymbol{r}_c)/2 \quad \text{(S2)}$$

$$= G_b(\boldsymbol{r}_c) + V_b(\boldsymbol{r}_c)/2 \quad \text{(S2')}$$

Interactions are classified by the signs of $\nabla^2\rho_b(\boldsymbol{r}_c)$ and $H_b(\boldsymbol{r}_c)$. Interactions in the region of $\nabla^2\rho_b(\boldsymbol{r}_c) < 0$ are called shared-shell (SS) interactions and they are closed-shell (CS) interactions for $\nabla^2\rho_b(\boldsymbol{r}_c) > 0$. $H_b(\boldsymbol{r}_c)$ must be negative when $\nabla^2\rho_b(\boldsymbol{r}_c) < 0$, since $H_b(\boldsymbol{r}_c)$ are larger than $(\hbar^2/8m)\nabla^2\rho_b(\boldsymbol{r}_c)$ by $V_b(\boldsymbol{r}_c)/2$ with negative $V_b(\boldsymbol{r}_c)$ at all BCPs (eqn (S2)). Consequently, $\nabla^2\rho_b(\boldsymbol{r}_c) < 0$ and $H_b(\boldsymbol{r}_c) < 0$ for the SS interactions. The CS interactions are especially called *pure* CS interactions for $H_b(\boldsymbol{r}_c) > 0$ and $\nabla^2\rho_b(\boldsymbol{r}_c) > 0$, since electrons at BCPs are depleted and destabilized under the conditions.[S1a] Electrons in the intermediate region between SS and *pure* CS, which belong to CS, are locally depleted but stabilized at BCPs, since $\nabla^2\rho_b(\boldsymbol{r}_c) > 0$ but $H_b(\boldsymbol{r}_c) < 0$.[S1a] We call the interactions in this region *regular* CS,[S4,S5] when it is necessary to distinguish

from *pure* CS. The role of $\nabla^2\rho_b(\boldsymbol{r}_c)$ in the classification can be replaced by $H_b(\boldsymbol{r}_c) - V_b(\boldsymbol{r}_c)/2$, since $(\hbar^2/8m)\nabla^2\rho_b(\boldsymbol{r}_c) = H_b(\boldsymbol{r}_c) - V_b(\boldsymbol{r}_c)/2$ (eqn (S2)).

We proposed QTAIM-DFA by plotting $H_b(\boldsymbol{r}_c)$ versus $H_b(\boldsymbol{r}_c) - V_b(\boldsymbol{r}_c)/2$ (= $(\hbar^2/8m)\nabla^2\rho_b(\boldsymbol{r}_c)$),[S4a] after the proposal of $H_b(\boldsymbol{r}_c)$ versus $\nabla^2\rho_b(\boldsymbol{r}_c)$.[S4b] Both axes in the plot of the former are given in energy unit, therefore, distances on the (x, y) (= $(H_b(\boldsymbol{r}_c) - V_b(\boldsymbol{r}_c)/2, H_b(\boldsymbol{r}_c))$ plane can be expressed in the energy unit, which provides an analytical development. QTAIM-DFA can incorporate the classification of interactions by the signs of $\nabla^2\rho_b(\boldsymbol{r}_c)$ and $H_b(\boldsymbol{r}_c)$. Scheme S1 summarizes the QTAIM-DFA treatment. Interactions of *pure* CS appear in the first quadrant, those of *regular* CS in the forth quadrant and SS interactions do in the third quadrant. No interactions appear in the second one.



Scheme S1. QTAIM-DFA: Plot of $H_b(\boldsymbol{r}_c)$ versus $H_b(\boldsymbol{r}_c) - V_b(\boldsymbol{r}_c)/2$ for Weak to Strong Interactions

In our treatment, data for perturbed structures around fully optimized structures are also employed for the plots, together with the fully optimized ones (see Figure S1).[S4-S6] We proposed the concept of the "dynamic nature of interaction" originated from the perturbed structures. The behavior of interactions at the fully optimized structures corresponds to "the static nature of interactions", whereas that containing perturbed structures exhibit the "dynamic nature of interaction" as explained below. The method to generate the perturbed structures is discussed later. Plots of $H_b(\boldsymbol{r}_c)$ versus $H_b(\boldsymbol{r}_c) - V_b(\boldsymbol{r}_c)/2$ are analyzed employing the polar coordinate (R, θ) representation with (θ_p, κ_p) parameters.[S4a,S5,S6] Figure S1 explains the treatment. R in (R, θ) is defined by eqn (S3) and given in the energy unit. R corresponds to the energy for an interaction at BCP. The plots show a spiral stream, as a whole. θ in (R, θ) defined by eqn (S4), measured from the y-axis, controls the spiral stream of the plot. Each plot for an interaction shows a specific curve, which provides important information of the interaction (see Figure S1). The curve is expressed by θ_p and κ_p. While θ_p, defined by eqn (S5) and measured from the y-direction, corresponds to the tangent line of a plot, where θ_p is calculated employing data of the perturbed structures with a fully-optimized structure and κ_p is the curvature of the plot (eqn (S6)). While (R, θ) correspond to the static nature, (θ_p, κ_p) represent the dynamic nature of interactions. We call (R, θ) and (θ_p, κ_p) QTAIM-DFA parameters, whereas $\rho_b(\boldsymbol{r}_c)$, $\nabla^2\rho_b(\boldsymbol{r}_c)$, $G_b(\boldsymbol{r}_c)$, $V_b(\boldsymbol{r}_c)$, $H_b(\boldsymbol{r}_c)$ and $H_b(\boldsymbol{r}_c) - V_b(\boldsymbol{r}_c)/2$ belong to QTAIM functions. $k_b(\boldsymbol{r}_c)$, defined by eqn (S7), is an QTAIM function but it will be treated as if it were an QTAIM-DFA parameter, if suitable.

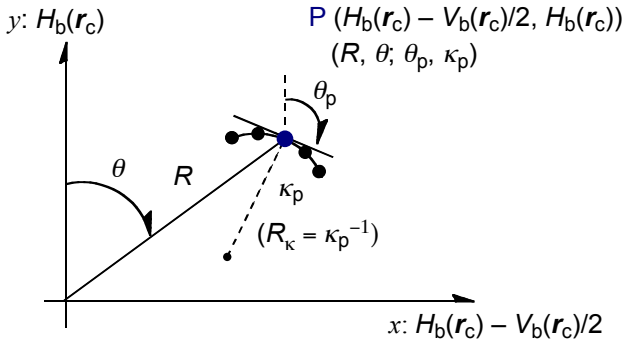


Figure S1. Polar (R, θ) coordinate representation of $H_b(\boldsymbol{r}_c)$ versus $H_b(\boldsymbol{r}_c) - V_b(\boldsymbol{r}_c)/2$, with ($\theta_p$, κ_p) parameters.

$$R = (x^2 + y^2)^{1/2} \quad \text{(S3)}$$

$$\theta = 90^\circ - \tan^{-1}(y/x) \quad \text{(S4)}$$

$$\theta_p = 90^\circ - \tan^{-1}(dy/dx) \quad \text{(S5)}$$

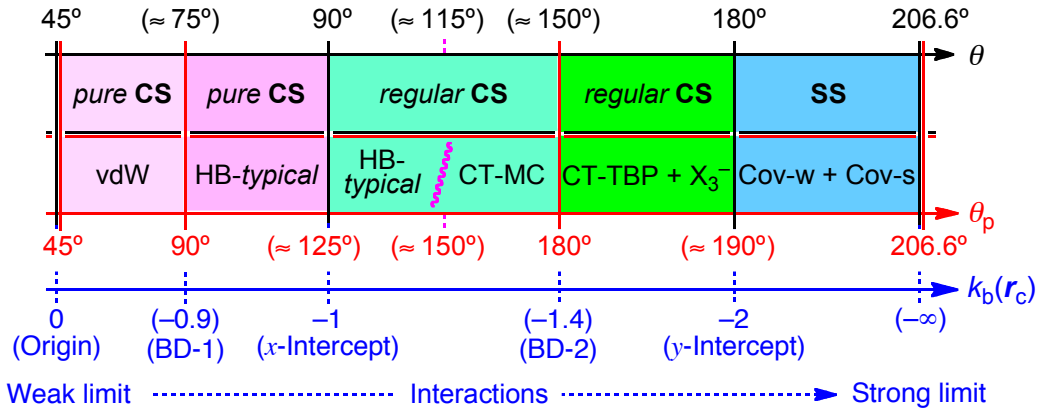
$$\kappa_p = \left|d^2y/dx^2\right| / [1 + (dy/dx)^2]^{3/2} \quad \text{(S6)}$$

$$k_b(\boldsymbol{r}_c) = V_b(\boldsymbol{r}_c)/G_b(\boldsymbol{r}_c) \quad \text{(S7)}$$

where $(x, y) = (H_b(\boldsymbol{r}_c) - V_b(\boldsymbol{r}_c)/2, H_b(\boldsymbol{r}_c))$

Criteria for Classification of Interactions: Behavior of Typical Interactions Elucidated by QTAIM-DFA

$H_b(\boldsymbol{r}_c)$ are plotted versus $H_b(\boldsymbol{r}_c) - V_b(\boldsymbol{r}_c)/2$ for typical interactions in vdW (van der Waals interactions), HB (hydrogen bonds), CT-MC (molecular complexes through charge transfer), X_3^- (trihalide ions), CT-TBP (trigonal bipyramidal adducts through charge-transfer), Cov-w (weak covalent bonds) and Cov-s (strong covalent bonds).[S4-S6] Rough criteria are obtained, after the analysis of the plots for the typical interactions according to eqns (S3)–(S7), by applying QTAIM-DFA. Scheme S2 shows the rough criteria, which are accomplished by the θ and θ_p values, together with the values of $k_b(\boldsymbol{r}_c)$. The criteria will be employed to discuss the nature of interactions in question, as a reference.



Scheme S2. Rough classification of interactions by θ and θ_p, together with $k_b(\boldsymbol{r}_c)$ (= $V_b(\boldsymbol{r}_c)/G_b(\boldsymbol{r}_c)$).

Table S1 Energies for the formation of the the EH_2 adducts with benzene π-system on the energy surface, together with the lowest two frequencies, optimized at the MP2, M06-2X and M06 levels with BSS-F[a]

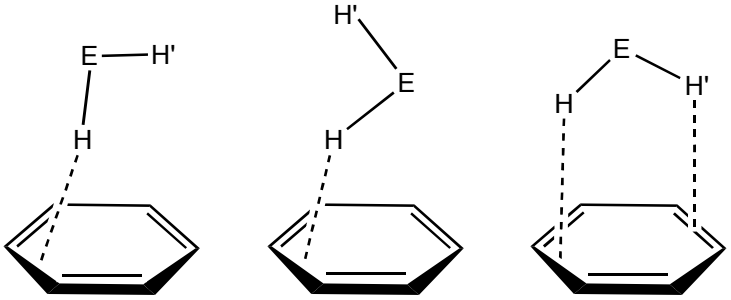
Species (X---Y) (symmetry: type)	E_{ES}[b] (au)	ν_1 (cm^{-1})	ν_2 (cm^{-1})
MP2 level			
HO–H---π(C_6H_6) (C_s: type Ia_{Bzn})	–307.906387	11.6 (A'')	50.7 (A')
HS–H---π(C_6H_6) (C_s: type Ib_{Bzn})	–630.482146	17.6 (A'')	21.6 (A')
HSe–H---π(C_6H_6) (C_s: type Ib_{Bzn})	–2632.888073	21.0 (A'')	37.5 (A')
HTe–H---π(C_6H_6) (C_s: type Ib_{Bzn})	–6844.626737	22.4 (A'')	65.5 (A')
OH_2---π(C_6H_6) (C_2: type II_{Bzn})[c]	–307.905756	–147.5 (B)	21.0 (A)
SH_2---π(C_6H_6) (C_2: type II_{Bzn})[c]	–630.481572	–110.4 (B)	33.9 (A)
SeH_2---π(C_6H_6) (C_2: type II_{Bzn})[c]	–2632.887136	–116.1 (B)	40.9 (A)
TeH_2---π(C_6H_6) (C_2: type II_{Bzn})[c]	–6844.624269	–89.4 (B)	14.5 (A)
SH_2---π(C_6H_6) (C_2: type II'_{Bzn})[d]	–630.481554	–112.2 (B)	–37.2 (A)
TeH_2---π(C_6H_6) (C_2: type II'_{Bzn})[d]	–6844.624252	–96.5 (B)	–39.9 (A)
M06-2X level			
HO–H---π(C_6H_6) (C_s: type Ia_{Bzn})	–308.630010	66.5 (A'')	74.4 (A')
HS–H---π(C_6H_6) (C_s: type Ia_{Bzn})	–631.586268	62.3 (A'')	70.0 (A')
HSe–H---π(C_6H_6) (C_1: type Ia_{Bzn})	–2634.946918	61.1 (A)	63.0 (A)
HTe–H---π(C_6H_6) (C_s: type Ia_{Bzn})	–6848.034500	62.0 (A')	64.4 (A'')
HS–H---π(C_6H_6) (C_s: type Ib_{Bzn})[c]	–631.586194	–135.5 (A'')	66.9 (A')
HSe–H---π(C_6H_6) (C_s: type Ib_{Bzn})	–2634.947299	62.0 (A')	62.5 (A'')
HTe–H---π(C_6H_6) (C_s: type Ib_{Bzn})	–6848.036017	62.2 (A'')	64.6 (A')
OH_2---π(C_6H_6) (C_2: type II_{Bzn})	–308.630031	65.1 (B)	72.4 (B)
SH_2---π(C_6H_6) (C_2: type II'_{Bzn})	–631.586072	56.2 (B)	62.5 (B)
SeH_2---π(C_6H_6) (C_2: type II_{Bzn})	–2634.946631	28.1 (B)	61.1 (B)
TeH_2---π(C_6H_6) (C_2: type II_{Bzn})	–6848.033902	36.8 (B)	55.5 (B)
M06 level			
HO–H---π(C_6H_6) (C_s: type Ia_{Bzn})	–308.539690	34.7 (A'')	53.7 (A')
HS–H---π(C_6H_6) (C_s: type Ia_{Bzn})	–631.502600	29.3 (A'')	67.4 (A')
HSe–H---π(C_6H_6) (C_s: type Ia_{Bzn})	–2634.74530	31.6 (A'')	52.1 (A')
HTe–H---π(C_6H_6) (C_s: type Ia_{Bzn})	–6847.371069	30.9 (A'')	45.0 (A')
HS–H---π(C_6H_6) (C_s: type Ib_{Bzn})	–631.502162	45.0 (A'')	57.9 (A')
HSe–H---π(C_6H_6) (C_s: type Ib_{Bzn})	–2634.745559	27.9 (A'')	63.7 (A')
HTe–H---π(C_6H_6) (C_s: type Ib_{Bzn})	–6847.372391	41.1 (A'')	54.5 (A')
OH_2---π(C_6H_6) (C_2: type II_{Bzn})	–308.539667	47.6 (B)	53.2 (B)
SH_2---π(C_6H_6) (C_1: type II_{Bzn})	–631.502589	38.9 (A)	46.0 (A)
SeH_2---π(C_6H_6) (C_2: type II'_{Bzn})	–2634.745336	41.5 (B)	49.9 (B)
TeH_2---π(C_6H_6) (C_2: type II_{Bzn})	–6847.371104	41.0 (B)	50.4 (B)

[a] See text for BSS-F. [b] On the energy surface. [c] One imaginary frequency being predicted for each. [d] Two imaginary frequencies being predicted for each.

Table S2 Structural parameters for the EH_2 adducts with benzene π-system, optimized by applying the counterpoise correction method at the MP2, M06-2X and M06 levels with BSS-F[a,b]

Species (X---Y) (symmetry: type)	r_1 (Å)	r_2 (Å)	r_3 (Å)	θ_1 (°)	θ_2 (°)	θ_3 (°)	ϕ_1 (°)	ϕ_2 (°)
MP2 level (Counterpoise)								
HO-H---π(C_6H_6) (C_s: type Ia_{Bzn})	2.9282	0.9633	0.9606	77.5	155.2	104.2	-82.6	-149.2
HS-H---π(C_6H_6) (C_s: type Ib_{Bzn})	2.6311	1.3387	1.3373	85.0	137.4	92.9	-87.1	-149.9
HSe-H---π(C_6H_6) (C_s: type Ib_{Bzn})	2.6981	1.4586	1.4584	83.9	125.7	92.0	-86.4	-149.8
HTe-H---π(C_6H_6) (C_s: type Ib_{Bzn})	2.8190	1.6563	1.6583	83.2	114.3	91.3	-94.0	-149.7
OH_2---π(C_6H_6) (C_2: type II_{Bzn})	3.4452	0.9619	0.9619	90.0	51.7	103.3	90.0	-30.0
SH_2---π(C_6H_6) (C_2: type II_{Bzn})	3.8381	1.3381	1.3381	90.0	45.8	91.6	90.0	-30.0
SeH_2---π(C_6H_6) (C_2: type II_{Bzn})	3.9427	1.4584	1.4584	90.0	45.3	90.6	90.0	-30.0
TeH_2---π(C_6H_6) (C_2: type II_{Bzn})	4.1281	1.6563	1.6563	90.0	45.2	90.4	90.0	-30.0
SH_2---π(C_6H_6) (C_2: type II'_{Bzn})	3.8378	1.3381	1.3381	90.0	45.8	91.6	90.0	0.0
TeH_2---π(C_6H_6) (C_2: type II'_{Bzn})	4.1290	1.6563	1.6563	90.0	45.2	90.4	90.0	0.0
M06-2X level (Counterpoise)								
HO-H---π(C_6H_6) (C_s: type Ia_{Bzn})	2.5731	0.9618	0.9600	78.9	126.4	103.7	-83.5	-149.3
	2.9450	0.9600	0.9618	74.5	99.0	103.7	-80.8	-148.7
HS-H---π(C_6H_6) (C_s: type Ia_{Bzn})	2.5579	1.3400	1.3367	84.6	145.6	92.0	-86.9	-149.8
HSe-H---π(C_6H_6) (C_s: type Ia_{Bzn})	2.5760	1.4685	1.4665	84.7	144.3	91.0	-86.9	-149.8
HTe-H---π(C_6H_6) (C_s: type Ia_{Bzn})	2.6410	1.6682	1.6667	84.7	138.2	91.6	-86.9	-149.8
HS-H---π(C_6H_6) (C_s: type Ib_{Bzn})	2.5542	1.3387	1.3383	86.6	129.4	92.9	-88.0	-149.9
HSe-H---π(C_6H_6) (C_s: type Ib_{Bzn})	2.5681	1.4683	1.4673	85.6	128.1	91.8	-87.5	-149.9
HTe-H---π(C_6H_6) (C_s: type Ib_{Bzn})	2.6954	1.6672	1.6690	84.5	117.0	91.9	-86.8	-149.8
OH_2---π(C_6H_6) (C_2: type II_{Bzn})	3.2349	0.9609	0.9609	90.0	51.8	103.6	90.0	-24.6
SH_2---π(C_6H_6) (C_2: type II'_{Bzn})	3.7224	1.3380	1.3380	90.1	45.8	91.5	89.9	7.5
SeH_2---π(C_6H_6) (C_2: type II_{Bzn})	3.8374	1.4679	1.4679	90.0	45.3	90.6	-90.0	30.0
TeH_2---π(C_6H_6) (C_2: type II_{Bzn})	4.0472	1.6671	1.6671	90.1	45.6	91.2	90.0	-19.8
M06 level (Counterpoise)								
HO-H---π(C_6H_6) (C_s: type Ia_{Bzn})	2.7425	0.9612	0.9595	75.5	124.5	103.9	-81.4	-148.9
HS-H---π(C_6H_6) (C_s: type Ia_{Bzn})	2.6601	1.3468	1.3429	78.5	146.6	91.8	-83.2	-149.3
HSe-H---π(C_6H_6) (C_s: type Ia_{Bzn})	2.6629	1.4735	1.4705	80.5	143.4	91.2	-84.4	-149.5
HTe-H---π(C_6H_6) (C_s: type Ia_{Bzn})	2.7857	1.6746	1.6721	79.5	132.8	91.0	-83.8	-149.4
HS-H---π(C_6H_6) (C_s: type Ib_{Bzn})	2.7024	1.3455	1.3433	85.2	125.8	92.5	-87.2	-149.9
HSe-H---π(C_6H_6) (C_s: type Ib_{Bzn})	2.7083	1.4718	1.4713	85.1	122.6	92.0	-87.1	-149.8
HTe-H---π(C_6H_6) (C_s: type Ib_{Bzn})	2.8841	1.6731	1.6754	84.6	111.9	91.2	-86.9	-149.8
OH_2---π(C_6H_6) (C_2: type II_{Bzn})	3.3870	0.9602	0.9602	90.0	52.0	103.9	90.0	-27.9
SH_2---π(C_6H_6) (C_2: type II_{Bzn})	3.7765	1.3455	1.3455	90.0	45.7	91.3	-90.0	20.7
SeH_2---π(C_6H_6) (C_1: type II'_{Bzn})	3.8872	1.4724	1.4724	90.0	45.4	90.8	90.0	0.0
TeH_2---π(C_6H_6) (C_2: type II_{Bzn})	4.1557	1.6728	1.6728	90.0	45.4	90.7	90.0	-11.7

[a] See text for BSS-F. [b] See Chart S1 and Scheme S3 for the structural parameters, which are the same as Chart 1 and Scheme 1, respectively.

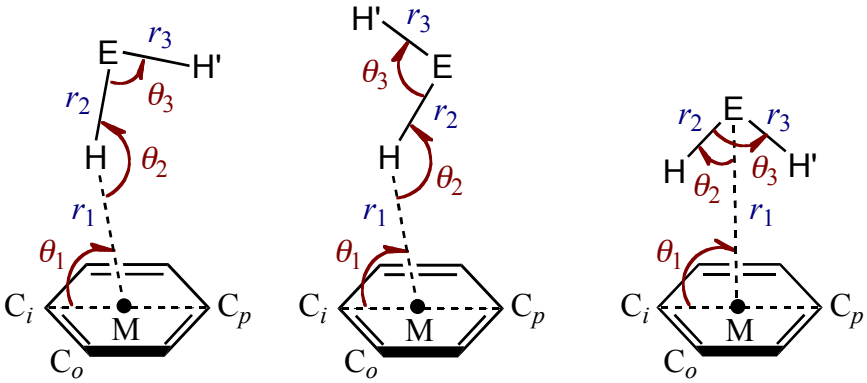


HE–H-∗-π(C_6H_6) type Ia_{Bzn} HE–H-∗-π(C_6H_6) type Ib_{Bzn} EH_2-∗-π(C_6H_6) type II_{Bzn}

E = O, S, Se and Te

(EH_2)-∗-π(C_6H_6): type Ia_{Bzn} + type Ib_{Bzn} + type II_{Bzn}

Chart S1. Structures expected for (EH_2)-∗-π(C_6H_6) (E = O, S, Se and Te).



ϕ_1(C_oC_iMH) ϕ_2(C_iMHE) ϕ_3(MHEH') type Ia_{Bzn}

ϕ_1(C_oC_iMH) ϕ_2(C_iMHE) ϕ_3(MHEH') type Ib_{Bzn}

ϕ_1(C_oC_iME) ϕ_2(C_iMEH) ϕ_3(MEHH') type II_{Bzn}

Scheme S3 Structural Parameters for (EH_2)---π(C_6H_6). The C_i atom in C_6H_6 is selected so as to the r(C_i---H) distance being shortest.

Table S3 The E_{CP} , E_{BSSE}, ΔE_{raw}, and ΔE_{BSSE} values for the EH_2 adducts with benzene π-system, evaluated by applying the counterpoise correction method at the MP2, M06-2X and M06 levels with BSS-F.[a]

Species (X---Y) (symmetry: type)	E_{CP}[b] (au)	E_{BSSE}[c] (au)	ΔE_{raw}[d] (kJ mol^{-1})	ΔE_{BSSE}[e] (kJ mol^{-1})
MP2 level (Counterpoise)				
HO-H---π(C_6H_6) (C_s: type Ia_{Bzn})	–307.903572	0.002458	-17.7	-11.2
HS-H---π(C_6H_6) (C_s: type Ib_{Bzn})	–630.479311	0.002629	-18.5	-11.5
HSe-H---π(C_6H_6) (C_s: type Ib_{Bzn})	–2632.884989	0.002884	-20.0	-12.5
HTe-H---π(C_6H_6) (C_s: type Ib_{Bzn})	–6844.621699	0.004591	-26.9	-14.8
OH_2---π(C_6H_6) (C_2: type II_{Bzn})	–307.903467	0.002166	-16.8	-11.1
SH_2---π(C_6H_6) (C_2: type II_{Bzn})	–630.479133	0.002329	-17.2	-11.1
SeH_2---π(C_6H_6) (C_2: type II_{Bzn})	–2632.884507	0.002490	-17.7	-11.2
TeH_2---π(C_6H_6) (C_2: type II_{Bzn})	–6844.620363	0.003643	-20.9	-11.3
SH_2---π(C_6H_6) (C_2: type II'_{Bzn})	–630.479136	0.002313	-17.2	-11.1
TeH_2---π(C_6H_6) (C_2: type II'_{Bzn})	–6844.620358	0.003644	-20.9	-11.3
M06-2X level (Counterpoise)				
HO–H---π(C_6H_6) (C_s: type Ia_{Bzn})	–308.629250	0.000754	-17.9	-15.9
HS–H---π(C_6H_6) (C_s: type Ia_{Bzn})	–631.585739	0.000524	-14.8	-13.4
HSe–H---π(C_6H_6) (C_s: type Ia_{Bzn})	–2634.946344	0.000512	-14.6	-13.2
HTe–H---π(C_6H_6) (C_s: type Ia_{Bzn})	–6848.034012	0.000485	-13.5	-12.2
HS–H---π(C_6H_6) (C_s: type Ib_{Bzn})	–631.585619	0.000565	-14.7	-13.2
HSe–H---π(C_6H_6) (C_s: type Ib_{Bzn})	–2634.946762	0.000534	-15.6	-14.2
HTe–H---π(C_6H_6) (C_s: type Ib_{Bzn})	–6848.035387	0.000624	-17.5	-15.9
OH_2---π(C_6H_6) (C_2: type II_{Bzn})	–308.629249	0.000774	-18.0	-15.9
SH_2---π(C_6H_6) (C_2: type II'_{Bzn})	–631.585394	0.000528	-14.3	-12.9
SeH_2---π(C_6H_6) (C_2: type II_{Bzn})	–2634.94612	0.000502	-13.8	-12.5
TeH_2---π(C_6H_6) (C_2: type II_{Bzn})	–6848.033441	0.000455	-11.9	-10.7
M06 level (Counterpoise)				
HO–H---π(C_6H_6) (C_s: type Ia_{Bzn})	–308.538894	0.000789	-13.8	-11.8
HS–H---π(C_6H_6) (C_s: type Ia_{Bzn})	–631.501951	0.000638	-12.3	-10.7
HSe–H---π(C_6H_6) (C_s: type Ia_{Bzn})	–2634.744695	0.000600	-12.3	-10.8
HTe–H---π(C_6H_6) (C_s: type Ia_{Bzn})	–6847.370505	0.000556	-11.6	-10.1
HS–H---π(C_6H_6) (C_s: type Ib_{Bzn})	–631.501535	0.000619	-11.3	-9.7
HSe–H---π(C_6H_6) (C_s: type Ib_{Bzn})	–2634.744927	0.000627	-13.1	-11.4
HTe–H---π(C_6H_6) (C_s: type Ib_{Bzn})	–6847.371694	0.000684	-15.1	-13.3
OH_2---π(C_6H_6) (C_2: type II_{Bzn})	–308.538861	0.000797	-13.8	-11.7
SH_2---π(C_6H_6) (C_2: type II_{Bzn})	–631.501977	0.000657	-12.5	-10.8
SeH_2---π(C_6H_6) (C_1: type II'_{Bzn})	–2634.744773	0.000572	-12.6	-11.0
TeH_2---π(C_6H_6) (C_2: type II_{Bzn})	–6847.370594	0.000505	-11.6	-10.3

[a] See text for BSS-F. [b] The counterpoise corrected energy. [c] Energy correction for basis set superposition error. [d] Energies for the formation of the complexes without considering E_{BSSE}. [e] Energies for the formation of the complexes corrected by E_{BSSE}.

Table S4. Lengths of Bond Paths (r_{BP}) with Components ($r_{BP\text{-}1}$ and $r_{BP\text{-}2}$) and the Corresponding Straight-line Distances (R_{SL}) in (EH_2)-∗-π(C_6H_6) (E = O, S, Se and Te), Evaluated at the MP2, M06-2X and M06 Levels with BSS-F[a,b]

Species (X---Y) (symmetry: type)	$r_{BP\text{-}1}$ (Å)	$r_{BP\text{-}2}$ (Å)	r_{BP} (Å)	R_{SL} (Å)
MP2 level				
HO-H-∗-π (C_s: type Ia_{Bzn})	0.9491	1.5640	2.5131	2.4862
HS-H-∗-π (C_s: type Ib_{Bzn})	1.0499	1.6026	2.6526	2.6356
HSe-H-∗-π (C_s: type Ib_{Bzn})	1.0785	1.6010	2.6795	2.6650
HTe-H-∗-π (C_s: type Ib_{Bzn})	1.1683	1.6294	2.7978	2.7814
HHTe-∗-π (C_s: type Ib_{Bzn})	1.8733	1.5979	3.4712	3.4705
OH_2-∗-π (C_2: type II_{Bzn})	1.1288	2.3613	3.4901	2.8465
SH_2-∗-π (C_2: type II_{Bzn})	1.1587	2.3530	3.5116	2.8902
SeH_2-∗-π (C_2: type II_{Bzn})	1.1633	2.3377	3.5010	2.8843
TeH_2-∗-π (C_2: type II_{Bzn})	1.1836	2.3173	3.5009	2.8854
M06-2X level				
HO-H-∗-π (C_s: type Ia_{Bzn})	1.0050	1.5988	2.6039	2.5729
(weaker π-HB	1.2693	1.6631	2.9324	2.7935)
H_2S-∗-π (C_s: type Ia_{Bzn})	1.0679	1.6340	2.7019	2.6862
H_2Se-∗-π (C_1: type Ia_{Bzn})	1.0808	1.6254	2.7062	2.6924
H_2Te-∗-π (C_s: type Ia_{Bzn})	1.1328	1.6461	2.7789	2.7671
HS-H-∗-π (C_s: type Ib_{Bzn})	1.1002	1.6585	2.7587	2.7416
(HHS-∗-π	2.1813	1.6435	3.8247	3.4525)
HSe-H-∗-π (C_s: type Ib_{Bzn})	1.1025	1.6373	2.7398	2.7253
(weaker π-HB	1.6235	1.6573	3.2809	2.9211)
HTe-H-∗-π (C_s: type Ib_{Bzn})	1.1763	1.6591	2.8354	2.8206
(HHTe-∗-π	1.9324	1.6560	3.5884	3.5768)
OH_2-∗-π (C_2: type II_{Bzn})	1.0802	2.0777	3.1578	2.7411
SH_2-∗-π (C_2: type II'_{Bzn})	1.1359	1.7253	2.8612	2.8102
SeH_2-∗-π (C_2: type II_{Bzn})	1.1538	1.6573	2.8111	2.7893
TeH_2-∗-π (C_2: type II_{Bzn})	1.2067	1.8438	3.0504	2.9027

[a] See "Methodological Details for Calculations" for BSSs. [b] See text for $r_{BP\text{-}1}$ and $r_{BP\text{-}2}$, where $r_{BP} = r_{BP\text{-}1} + r_{BP\text{-}2}$.

(To be continued.)

Species (X---Y) (symmetry: type)	r_{BP-1} (Å)	r_{BP-2} (Å)	r_{BP} (Å)	R_{SL} (Å)
M06 level				
HO-H-∗-π (C_s: type Ia_{Bzn})	1.0101	1.5922	2.6023	2.5729
(weaker π-HB	1.2520	1.6598	2.9118	2.7935)
HS-H-∗-π (C_s: type Ia_{Bzn})	1.0471	1.5936	2.6407	2.6266
HSe-H-∗-π (C_s: type Ia_{Bzn})	1.0809	1.6039	2.6848	2.6720
HTe-H-∗-π (C_s: type Ia_{Bzn})	1.1460	1.6327	2.7787	2.7672
(weaker π-HB	1.4519	1.7942	3.2461	3.1673)
HS-H-∗-π (C_s: type Ib_{Bzn})	1.1542	1.7012	2.8554	2.8387
(HHS-∗-π	2.0975	1.7229	3.8204	3.5770)
HSe-H-∗-π (C_s: type Ib_{Bzn})	1.1721	1.6853	2.8574	2.8422
(HHSe-∗-π	2.0352	1.7156	3.7508	3.5993)
HTe-H-∗-π (C_s: type Ib_{Bzn})	1.2834	1.7424	3.0258	3.0087
(HHTe-∗-π	1.9343	1.6888	3.6231	3.6222)
OH_2-∗-π (C_2: type II_{Bzn})	1.1472	2.2005	3.3477	2.8835
SH_2-∗-π (C_1: type II_{Bzn})	1.1708	1.8427	3.0136	2.8827
SeH_2-∗-π (C_2: type II'_{Bzn})	1.1767	1.7102	2.8870	2.8525
TeH_2-∗-π (C_2: type II_{Bzn})	1.2551	1.7874	3.0425	2.9784

[a] See "Methodological Details for Calculations" for BSSs. [b] See text for r_{BP-1} and r_{BP-2}, where $r_{BP} = r_{BP-1} + r_{BP-2}$.

Optimized structures given by Cartesian coordinates

Structures were optimized employing the Gaussian 09 program.[S7] Several types of basis set systems (BSSs: BSS-A, BSS-B, BSS-C, BSS-D, BSS-E and BSS-F) were examined for the evaluation. Table S4 summarizes the BSSs. The basis set for I of the 6-311G* type[S8] was obtained from EMSL Basis Set Exchange Library.[S9,S10] Higher basis set for I of the (7433211/743111/7411/2 + 1s1p1d1f) type was from Sapporo Basis Set Factory.[S11] The diffusion functions of the *sp* parts for I in (7433211/743111/7411/2 + 1s1p1d1f)[S12] were diverted as those of the *sp* type for the 6-311G* basis set of I, since the diffusion functions could not be found for 6-311G* of I. The Møller-Plesset second order energy correlation (MP2) level is applied to the calculations.[S13] The optimized structures were confirmed by the frequency analysis. The abbreviated notation of MP2/BSS-X (X = A, B, C, D, E and F) will also be used to describe the calculation methods employing BSS-X at the MP2 level, if suitable.

Table S5 Basis set systems employed for the calculations

Method	C, H	F, Cl, Br	I
BSS-A	6-311G(d, p)	6-311G(d)	(5211111111/411111111/31111)[a]
BSS-B	6-311G(d, p)	6-311+G(d)	(5211111111/411111111/31111 + 1s1p)[a,b]
BSS-C	6-311G(d, p)	6-311G(3d)	(7433211/743111/7411/2 + 1s1p1d1f)[c]
BSS-D	6-311G(d, p)	6-311G(3df)	(7433211/743111/7411/2 + 1s1p1d1f)[c]
BSS-E	6-311G(d, p)	6-311+G(3df)	(7433211/743111/7411/2 + 1s1p1d1f)[c]
BSS-F	6-311++G(d, p)	6-311+G(3df)	(7433211/743111/7411/2 + 1s1p1d1f)[c]

[a] The basis set of the 6-311G* type for I was obtained through EMSL Basis Set Exchange Library.[S3,S4] [b] Diffusion functions of the 1s1p parts in (7433211/743111/7411/2 + 1s1p1d1f)[S5] being employed as the diffusion functions of the 1s1p type for (5211111111/411111111/31111). [c] The higher basis set of the (7433211/743111/7411/2 + 1s1p1d1f) type for I was obtained from Sapporo Basis Set Factory.[S5]

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MP2/BSS-F C, H : 6-311++G(d,p), O : 6-311+G(3df)
Adduct H-OH---π(C_6H_6)
Symmetry C_s
energy E = -307.906387 au
Standard orientation

6	0	-0.621401	-1.260462	0.700630
6	0	-0.621401	-1.260462	-0.700630
6	0	-0.621401	-0.047508	1.401382
6	0	-0.621401	-0.047508	-1.401382
6	0	-0.621751	1.166072	0.700808
6	0	-0.621751	1.166072	-0.700808
1	0	-0.623998	-2.201468	1.244318
1	0	-0.623998	-2.201468	-1.244318
1	0	-0.618592	-0.046843	2.487893
1	0	-0.618592	-0.046843	-2.487893
1	0	-0.618596	2.107113	1.243924
1	0	-0.618596	2.107113	-1.243924
1	0	1.727273	0.351651	0.000000
8	0	2.688595	0.286512	0.000000
1	0	2.860984	-0.658572	0.000000

MP2/BSS-F C, H : 6-311++G(d,p), S : 6-311+G(3df)
Adduct H-SH---π(C_6H_6)
Symmetry C_s
energy E = -630.4821464 au
Standard orientation

6	0	-1.077892	-1.307124	0.700866
6	0	-1.077892	-1.307124	-0.700866
6	0	-1.079338	-0.093885	1.401277
6	0	-1.079338	-0.093885	-1.401277
6	0	-1.079338	1.118876	0.700433
6	0	-1.079338	1.118876	-0.700433
1	0	-1.079187	-2.248405	1.244252
1	0	-1.079187	-2.248405	-1.244252
1	0	-1.075781	-0.093684	2.487898
1	0	-1.075781	-0.093684	-2.487898
1	0	-1.077930	2.059964	1.243895
1	0	-1.077930	2.059964	-1.243895
1	0	1.354077	-0.291363	0.000000
16	0	2.546051	0.317645	0.000000
1	0	3.213721	-0.841104	0.000000

MP2/BSS-F C, H : 6-311++G(d,p), Se : 6-311+G(3df)
Adduct H-SeH---π(C_6H_6)
Symmetry C_s
energy E = -2632.8880725 au
Standard orientation

6	0	-1.638609	-1.510133	0.700947
6	0	-1.638609	-1.510133	-0.700947
6	0	-1.643023	-0.297139	1.401288
6	0	-1.643023	-0.297139	-1.401288
6	0	-1.643023	0.915624	0.700510

6	0	-1.643023	0.915624	-0.700510
1	0	-1.638871	-2.451523	1.244322
1	0	-1.638871	-2.451523	-1.244322
1	0	-1.640764	-0.296698	2.487937
1	0	-1.640764	-0.296698	-2.487937
1	0	-1.644472	1.856787	1.244055
1	0	-1.644472	1.856787	-1.244055
1	0	0.872193	-0.616713	0.000000
34	0	1.914692	0.402973	0.000000
1	0	2.972341	-0.601728	0.000000

MP2/BSS-F C, H : 6-311++G(d,p), Te : 74331111/7431111/74111/21
Adduct H-TeH---π(C_6H_6)
Symmetry C_s
energy E = -6844.6267373 au
Standard orientation

6	0	-1.949153	-1.792328	0.701028
6	0	-1.949153	-1.792328	-0.701028
6	0	-1.958868	-0.580251	1.401901
6	0	-1.958868	-0.580251	-1.401901
6	0	-1.958868	0.632859	0.700923
6	0	-1.958868	0.632859	-0.700923
1	0	-1.947306	-2.733929	1.244056
1	0	-1.947306	-2.733929	-1.244056
1	0	-1.958159	-0.579470	2.488615
1	0	-1.958159	-0.579470	-2.488615
1	0	-1.961782	1.574281	1.244336
1	0	-1.961782	1.574281	-1.244336
1	0	0.702992	-0.954180	0.000000
52	0	1.508804	0.492149	0.000000
1	0	2.976340	-0.282677	0.000000

MP2/BSS-F C, H : 6-311++G(d,p), O : 6-311+G(3df)
Adduct OH_2---π(C_6H_6)
Symmetry C_2
energy E = -307.9057564 au
Standard orientation

6	0	-1.212893	0.700779	-0.614927
6	0	-1.212893	-0.700777	-0.614927
6	0	0.000000	1.401519	-0.614481
6	0	0.000000	-1.401519	-0.614481
6	0	1.212893	0.700777	-0.614927
6	0	1.212893	-0.700779	-0.614927
1	0	-2.154038	1.244433	-0.621935
1	0	-2.154039	-1.244431	-0.621944
1	0	0.000000	2.488040	-0.614444
1	0	0.000000	-2.488040	-0.614444
1	0	2.154039	1.244431	-0.621944
1	0	2.154038	-1.244433	-0.621935
1	0	0.752922	0.000348	2.105478
8	0	0.000000	0.000000	2.704714
1	0	-0.752922	-0.000348	2.105478

MP2/BSS-F C, H : 6-311++G(d,p), S : 6-311+G(3df)
Adduct SH_2---$\pi(C_6H_6)$
Symmetry C_2
energy E = -630.4815717 au
Standard orientation

6	0	-1.212661	0.700648	-1.086660
6	0	-1.212661	-0.700646	-1.086659
6	0	0.000000	1.401330	-1.086567
6	0	0.000000	-1.401330	-1.086567
6	0	1.212661	0.700646	-1.086659
6	0	1.212661	-0.700648	-1.086660
1	0	-2.153934	1.244330	-1.091880
1	0	-2.153935	-1.244327	-1.091888
1	0	0.000001	2.487945	-1.084576
1	0	-0.000001	-2.487945	-1.084576
1	0	2.153935	1.244327	-1.091888
1	0	2.153934	-1.244330	-1.091880
1	0	0.957992	0.000472	1.705887
16	0	0.000000	0.000000	2.640222
1	0	-0.957992	-0.000472	1.705887

MP2/BSS-F C, H : 6-311++G(d,p), Se : 6-311+G(3df)
Adduct SeH_2---$\pi(C_6H_6)$
Symmetry C_2
energy E = -2632.8871355 au
Standard orientation

6	0	-1.212611	0.700656	-1.736397
6	0	-1.212611	-0.700653	-1.736396
6	0	0.000000	1.401334	-1.736596
6	0	0.000000	-1.401334	-1.736596
6	0	1.212611	0.700653	-1.736396
6	0	1.212611	-0.700656	-1.736397
1	0	-2.153909	1.244363	-1.742335
1	0	-2.153910	-1.244361	-1.742343
1	0	0.000000	2.487982	-1.735241
1	0	0.000000	-2.487982	-1.735241
1	0	2.153910	1.244361	-1.742343
1	0	2.153909	-1.244363	-1.742335
1	0	1.035002	0.000532	1.056031
34	0	0.000000	0.000000	2.083542
1	0	-1.035002	-0.000532	1.056031

MP2/BSS-F C, H : 6-311++G(d,p), Te : 74331111/7431111/74111/21
Adduct TeH_2---$\pi(C_6H_6)$
Symmetry C_2
energy E = -6844.6242687 au
Standard orientation

6	0	-1.212603	0.700646	-2.206398
6	0	-1.212603	-0.700644	-2.206397
6	0	0.000000	1.401370	-2.205621

6	0	0.000000	-1.401370	-2.205621
6	0	1.212603	0.700644	-2.206397
6	0	1.212603	-0.700646	-2.206398
1	0	-2.153979	1.244291	-2.211354
1	0	-2.153980	-1.244288	-2.211362
1	0	0.000001	2.488131	-2.205238
1	0	-0.000001	-2.488131	-2.205238
1	0	2.153980	1.244288	-2.211362
1	0	2.153979	-1.244291	-2.211354
1	0	1.174439	0.000621	0.592519
52	0	0.000000	0.000000	1.759459
1	0	-1.174439	-0.000621	0.592519

MP2/BSS-F C, H : 6-311++G(d,p), S : 6-311+G(3df)
Adduct SH_2---π(C_6H_6)
Symmetry C_2
energy E = -630.4815543 au
Standard orientation

6	0	0.000000	1.400199	-1.086877
6	0	-1.213613	0.700124	-1.087463
6	0	1.213613	0.700121	-1.087464
6	0	-1.213613	-0.700121	-1.087464
6	0	1.213613	-0.700124	-1.087463
6	0	0.000000	-1.400199	-1.086877
1	0	0.000000	2.487359	-1.094887
1	0	-2.154792	1.243423	-1.087782
1	0	2.154793	1.243419	-1.087794
1	0	-2.154793	-1.243419	-1.087794
1	0	2.154792	-1.243423	-1.087782
1	0	0.000000	-2.487359	-1.094887
1	0	-0.000692	-0.957868	1.707284
16	0	0.000000	0.000000	2.641750
1	0	0.000692	0.957868	1.707284

MP2/BSS-F C, H : 6-311++G(d,p), Te : 74331111/7431111/74111/21
Adduct TeH_2---π(C_6H_6)
Symmetry C_2
energy E = -6844.6242523 au
Standard orientation

6	0	0.000000	1.400098	-2.208554
6	0	-1.213630	0.700089	-2.208828
6	0	1.213630	0.700086	-2.208830
6	0	-1.213630	-0.700086	-2.208830
6	0	1.213630	-0.700089	-2.208828
6	0	0.000000	-1.400098	-2.208554
1	0	0.000000	2.487299	-2.216518
1	0	-2.154873	1.243520	-2.209818
1	0	2.154874	1.243517	-2.209828
1	0	-2.154874	-1.243517	-2.209828
1	0	2.154873	-1.243520	-2.209818
1	0	0.000000	-2.487299	-2.216518
1	0	-0.000813	-1.174227	0.594423

52	0	0.000000	0.000000	1.761500
1	0	0.000813	1.174227	0.594423

M06-2X/BSS-F C, H : 6-311++G(d,p), O : 6-311+G(3df)
Adduct HO-H---π(C_6H_6)
Symmetry C_s
energy E = -308.6300096 au
Standard orientation

6	0	0.599550	1.189072	0.696431
6	0	0.599550	1.189072	-0.696431
6	0	0.595134	-0.016300	1.392857
6	0	0.595134	-0.016300	-1.392857
6	0	0.595134	-1.222008	0.696690
6	0	0.595134	-1.222008	-0.696690
1	0	0.603965	2.127185	1.239165
1	0	0.603965	2.127185	-1.239165
1	0	0.590028	-0.016379	2.476145
1	0	0.590028	-0.016379	-2.476145
1	0	0.594293	-2.160213	1.238986
1	0	0.594293	-2.160213	-1.238986
1	0	-1.897834	-0.585697	0.000000
8	0	-2.622224	0.047088	0.000000
1	0	-2.178765	0.898629	0.000000

M06-2X/BSS-F C, H : 6-311++G(d,p), S : 6-311+G(3df)
Adduct HS-H---π(C_6H_6)
Symmetry C_s
energy E = -631.5862675 au
Standard orientation

6	0	1.085125	1.094316	0.696172
6	0	1.085125	1.094316	-0.696172
6	0	1.082544	-0.111009	1.392474
6	0	1.082544	-0.111009	-1.392474
6	0	1.082544	-1.316591	0.696459
6	0	1.082544	-1.316591	-0.696459
1	0	1.085433	2.032329	1.239083
1	0	1.085433	2.032329	-1.239083
1	0	1.076266	-0.110906	2.475852
1	0	1.076266	-0.110906	-2.475852
1	0	1.080077	-2.254823	1.238683
1	0	1.080077	-2.254823	-1.238683
1	0	-1.444223	-0.404810	0.000000
16	0	-2.625401	0.227731	0.000000
1	0	-2.035477	1.427314	0.000000

M06-2X/BSS-F C, H : 6-311++G(d,p), Se : 6-311+G(3df)
Adduct HSe-H---π(C_6H_6)
Symmetry C_1
energy E = -2634.9469181 au
Standard orientation

6	0	-1.595104	1.239032	-0.696138

6	0	-1.595104	1.239032	0.696139
6	0	-1.754742	0.044591	-1.392815
6	0	-1.754740	0.044591	1.392817
6	0	-1.915921	-1.149937	-0.696456
6	0	-1.915920	-1.149937	0.696459
1	0	-1.467949	2.169002	-1.237951
1	0	-1.467948	2.169002	1.237952
1	0	-1.748571	0.043904	-2.476188
1	0	-1.748569	0.043905	2.476190
1	0	-2.039008	-2.080695	-1.237638
1	0	-2.039007	-2.080694	1.237641
1	0	0.708899	-0.550459	-0.000001
34	0	2.098260	-0.077536	-0.000001
1	0	1.650505	1.318044	0.000000

M06-2X/BSS-F C, H : 6-311++G(d,p), Te : 74331111/7431111/74111/21
Adduct HTe-H---π(C_6H_6)
Symmetry C_s
energy E = -6848.0344995 au
Standard orientation

6	0	2.209469	0.818810	0.696120
6	0	2.209469	0.818810	-0.696120
6	0	2.207380	-0.386273	1.392263
6	0	2.207380	-0.386273	-1.392263
6	0	2.207380	-1.591794	0.696293
6	0	2.207380	-1.591794	-0.696293
1	0	2.206821	1.756951	1.238913
1	0	2.206821	1.756951	-1.238913
1	0	2.201602	-0.386005	2.475742
1	0	2.201602	-0.386005	-2.475742
1	0	2.205514	-2.530072	1.238552
1	0	2.205514	-2.530072	-1.238552
1	0	-0.405711	-0.681518	0.000000
52	0	-1.759376	0.293029	0.000000
1	0	-0.825322	1.673343	0.000000

M06-2X/BSS-F C, H : 6-311++G(d,p), S : 6-311+G(3df)
Adduct HS-H---π(C_6H_6)
Symmetry C_s
energy E = -631.5861935 au
Standard orientation

6	0	-1.031191	-1.421533	0.696706
6	0	-1.031191	-1.421533	-0.696706
6	0	-1.033012	-0.216116	1.392393
6	0	-1.033012	-0.216116	-1.392393
6	0	-1.033012	0.989319	0.696011
6	0	-1.033012	0.989319	-0.696011
1	0	-1.029477	-2.359919	1.238805
1	0	-1.029477	-2.359919	-1.238805
1	0	-1.026311	-0.215430	2.475790
1	0	-1.026311	-0.215430	-2.475790
1	0	-1.024906	1.927396	1.238249

1	0	-1.024906	1.927396	-1.238249
1	0	1.511961	-0.397350	0.000000
16	0	2.398169	0.606293	0.000000
1	0	3.445304	-0.227479	0.000000

M06-2X/BSS-F C, H : 6-311++G(d,p), Se : 6-311+G(3df)
Adduct HSe-H---π(C_6H_6)
Symmetry C_s
energy E = -2634.9472993 au
Standard orientation

6	0	-1.636400	-1.570657	0.696715
6	0	-1.636400	-1.570657	-0.696715
6	0	-1.638099	-0.365419	1.392489
6	0	-1.638099	-0.365419	-1.392489
6	0	-1.638099	0.840097	0.696107
6	0	-1.638099	0.840097	-0.696107
1	0	-1.633504	-2.509068	1.238753
1	0	-1.633504	-2.509068	-1.238753
1	0	-1.631462	-0.364829	2.475873
1	0	-1.631462	-0.364829	-2.475873
1	0	-1.632635	1.778179	1.238525
1	0	-1.632635	1.778179	-1.238525
1	0	0.907419	-0.592741	0.000000
34	0	1.906643	0.482851	0.000000
1	0	3.013095	-0.481019	0.000000

M06-2X/BSS-F C, H : 6-311++G(d,p), Te : 74331111/7431111/74111/21
Adduct HTe-H---π(C_6H_6)
Symmetry C_s
energy E = -6848.0360172 au
Standard orientation

6	0	-2.016651	-1.796609	0.696648
6	0	-2.016651	-1.796609	-0.696648
6	0	-2.016651	-0.591960	1.392556
6	0	-2.016651	-0.591960	-1.392556
6	0	-2.016818	0.613916	0.696323
6	0	-2.016818	0.613916	-0.696323
1	0	-2.014350	-2.735074	1.238561
1	0	-2.014350	-2.735074	-1.238561
1	0	-2.009646	-0.591185	2.475979
1	0	-2.009646	-0.591185	-2.475979
1	0	-2.013014	1.552097	1.239017
1	0	-2.013014	1.552097	-1.239017
1	0	0.658001	-0.901076	0.000000
52	0	1.558184	0.501869	0.000000
1	0	2.991892	-0.351962	0.000000

M06-2X/BSS-F C, H : 6-311++G(d,p), O : 6-311+G(3df)
Adduct OH_2---π(C_6H_6)
Symmetry C_2
energy E = -308.6300305 au

Standard orientation

6	0	0.000000	1.392038	-0.595766
6	0	-1.206204	0.695190	-0.596495
6	0	1.206264	0.697128	-0.594198
6	0	-1.206264	-0.697128	-0.594198
6	0	1.206204	-0.695190	-0.596495
6	0	0.000000	-1.392038	-0.595766
1	0	-0.000177	2.475734	-0.597457
1	0	-2.144877	1.236922	-0.599524
1	0	2.144033	1.239535	-0.589828
1	0	-2.144033	-1.239535	-0.589828
1	0	2.144877	-1.236922	-0.599524
1	0	0.000177	-2.475734	-0.597457
1	0	0.407999	-0.635022	2.025145
8	0	0.000000	0.000000	2.620103
1	0	-0.407999	0.635022	2.025145

M06-2X/BSS-F C, H : 6-311++G(d,p), S : 6-311+G(3df)
Adduct SH_2---$\pi(C_6H_6)$
Symmetry C_2
energy E = -631.5860723 au
Standard orientation

6	0	-1.205350	0.695585	-1.082284
6	0	-1.205480	-0.696998	-1.080160
6	0	0.000000	1.392405	-1.078795
6	0	0.000000	-1.392405	-1.078795
6	0	1.205480	0.696998	-1.080160
6	0	1.205350	-0.695585	-1.082284
1	0	-2.143949	1.237827	-1.085766
1	0	-2.143446	-1.239632	-1.077827
1	0	-0.000186	2.475861	-1.073747
1	0	0.000186	-2.475861	-1.073747
1	0	2.143446	1.239632	-1.077827
1	0	2.143949	-1.237827	-1.085766
1	0	0.883868	-0.370972	1.690514
16	0	0.000000	0.000000	2.624282
1	0	-0.883868	0.370972	1.690514

M06-2X/BSS-F C, H : 6-311++G(d,p), Se : 6-311+G(3df)
Adduct SeH_2---$\pi(C_6H_6)$
Symmetry C_2
energy E = -2634.9466306 au
Standard orientation

6	0	-1.205203	0.696334	-1.736479
6	0	-1.205203	-0.696334	-1.736480
6	0	0.000000	1.392502	-1.732770
6	0	0.000000	-1.392502	-1.732770
6	0	1.205203	0.696334	-1.736480

6	0	1.205203	-0.696334	-1.736479
1	0	-2.143456	1.238940	-1.737171
1	0	-2.143457	-1.238940	-1.737169
1	0	0.000000	2.475887	-1.725929
1	0	0.000000	-2.475887	-1.725929
1	0	2.143457	1.238940	-1.737169
1	0	2.143456	-1.238940	-1.737171
1	0	1.042454	0.000058	1.048037
34	0	0.000000	0.000000	2.081565
1	0	-1.042454	-0.000058	1.048037

M06-2X/BSS-F C, H : 6-311++G(d,p), Te : 74331111/7431111/74111/21
Adduct TeH_2---$\pi(C_6H_6)$
Symmetry C_2
energy E = -6848.0339018 au
Standard orientation

6	0	1.205217	-0.696509	-2.241838
6	0	1.205113	0.695868	-2.242920
6	0	0.000000	-1.392271	-2.239033
6	0	0.000000	1.392271	-2.239033
6	0	-1.205113	-0.695868	-2.242920
6	0	-1.205217	0.696509	-2.241838
1	0	2.143410	-1.239055	-2.239937
1	0	2.143530	1.238340	-2.243325
1	0	-0.000124	-2.475754	-2.232518
1	0	0.000124	2.475754	-2.232518
1	0	-2.143530	-1.238340	-2.243325
1	0	-2.143410	1.239055	-2.239937
1	0	-1.171236	-0.213568	0.619246
52	0	0.000000	0.000000	1.786126
1	0	1.171236	0.213568	0.619246

M06/BSS-F C, H : 6-311++G(d,p), O : 6-311+G(3df)
Adduct HO-H---$\pi(C_6H_6)$
Symmetry C_s
energy E = -308.6300096 au
Standard orientation

6	0	0.599548	1.189067	0.696431
6	0	0.599548	1.189067	-0.696431
6	0	0.595135	-0.016305	1.392858
6	0	0.595135	-0.016305	-1.392858
6	0	0.595135	-1.222014	0.696690
6	0	0.595135	-1.222014	-0.696690
1	0	0.603960	2.127182	1.239162
1	0	0.603960	2.127182	-1.239162
1	0	0.590024	-0.016385	2.476145
1	0	0.590024	-0.016385	-2.476145
1	0	0.594289	-2.160219	1.238987
1	0	0.594289	-2.160219	-1.238987
1	0	-1.897831	-0.585674	0.000000
8	0	-2.622221	0.047110	0.000000
1	0	-2.178764	0.898652	0.000000

M06/BSS-F C, H : 6-311++G(d,p), S : 6-311+G(3df)
Adduct HS-H---π(C_6H_6)
Symmetry C_s
energy E = -631.5026003 au
Standard orientation

6	0	-1.122050	-1.254147	0.694663
6	0	-1.122050	-1.254147	-0.694663
6	0	-1.122050	-0.052034	1.389945
6	0	-1.122050	-0.052034	-1.389945
6	0	-1.125374	1.150765	0.694812
6	0	-1.125374	1.150765	-0.694812
1	0	-1.121639	-2.194773	1.237421
1	0	-1.121639	-2.194773	-1.237421
1	0	-1.117247	-0.051806	2.475519
1	0	-1.117247	-0.051806	-2.475519
1	0	-1.126602	2.091429	1.237516
1	0	-1.126602	2.091429	-1.237516
1	0	1.448420	0.626841	0.000000
16	0	2.713881	0.166135	0.000000
1	0	2.294154	-1.109698	0.000000

M06/BSS-F C, H : 6-311++G(d,p), Se : 6-311+G(3df)
Adduct HSe-H---π(C_6H_6)
Symmetry C_s
energy E = -2634.745301 au
Standard orientation

6	0	1.787013	1.151866	0.694597
6	0	1.787013	1.151866	-0.694597
6	0	1.784285	-0.050222	1.389909
6	0	1.784285	-0.050222	-1.389909
6	0	1.784285	-1.252894	0.694799
6	0	1.784285	-1.252894	-0.694799
1	0	1.788072	2.092494	1.237467
1	0	1.788072	2.092494	-1.237467
1	0	1.779453	-0.050233	2.475499
1	0	1.779453	-0.050233	-2.475499
1	0	1.783352	-2.193591	1.237436
1	0	1.783352	-2.193591	-1.237436
1	0	-0.804576	-0.591614	0.000000
34	0	-2.136108	0.039043	0.000000
1	0	-1.536497	1.381790	0.000000

M06/BSS-F C, H : 6-311++G(d,p), Te : 74331111/7431111/74111/21
Adduct HTe-H---π(C_6H_6)
Symmetry C_s
energy E = -6847.3710687 au
Standard orientation

6	0	2.265057	0.992715	0.694555
6	0	2.265057	0.992715	-0.694555
6	0	2.262634	-0.209371	1.389804

6	0	2.262634	-0.209371	-1.389804
6	0	2.262634	-1.411886	0.694729
6	0	2.262634	-1.411886	-0.694729
1	0	2.265277	1.933446	1.237433
1	0	2.265277	1.933446	-1.237433
1	0	2.257991	-0.209193	2.475490
1	0	2.257991	-0.209193	-2.475490
1	0	2.261671	-2.352641	1.237347
1	0	2.261671	-2.352641	-1.237347
1	0	-0.439745	-0.816470	0.000000
52	0	-1.803044	0.155432	0.000000
1	0	-0.855778	1.533268	0.000000

M06/BSS-F C, H : 6-311++G(d,p), S : 6-311+G(3df)
Adduct HS-H---π(C_6H_6)
Symmetry C_s
energy E = -631.5021622 au
Standard orientation

6	0	-1.067909	-1.399078	0.694985
6	0	-1.067909	-1.399078	-0.694985
6	0	-1.068555	-0.196503	1.389783
6	0	-1.068555	-0.196503	-1.389783
6	0	-1.068555	1.005836	0.694440
6	0	-1.068555	1.005836	-0.694440
1	0	-1.068740	-2.339898	1.237484
1	0	-1.068740	-2.339898	-1.237484
1	0	-1.063505	-0.195954	2.475398
1	0	-1.063505	-0.195954	-2.475398
1	0	-1.062344	1.946419	1.236982
1	0	-1.062344	1.946419	-1.236982
1	0	1.613601	-0.467481	0.000000
16	0	2.480681	0.561373	0.000000
1	0	3.544918	-0.258677	0.000000

M06/BSS-F C, H : 6-311++G(d,p), Se : 6-311+G(3df)
Adduct HSe-H---π(C_6H_6)
Symmetry C_s
energy E = -2634.7455592 au
Standard orientation

6	0	-1.657976	-1.586192	0.695015
6	0	-1.657976	-1.586192	-0.695015
6	0	-1.659160	-0.383971	1.389948
6	0	-1.659160	-0.383971	-1.389948
6	0	-1.659160	0.818666	0.694583
6	0	-1.659160	0.818666	-0.694583
1	0	-1.657080	-2.527056	1.237387
1	0	-1.657080	-2.527056	-1.237387
1	0	-1.654146	-0.383396	2.475527
1	0	-1.654146	-0.383396	-2.475527
1	0	-1.655678	1.759276	1.237310
1	0	-1.655678	1.759276	-1.237310
1	0	1.030167	-0.663289	0.000000

34	0	1.926337	0.503963	0.000000
1	0	3.123727	-0.351132	0.000000

M06/BSS-F C, H : 6-311++G(d,p), Te : 74331111/7431111/74111/21
Adduct $HTe\text{-}H\text{---}\pi(C_6H_6)$
Symmetry C_s
energy E = -6847.372391 au
Standard orientation

6	0	-2.044980	-1.849653	0.694994
6	0	-2.044980	-1.849653	-0.694994
6	0	-2.044980	-0.648095	1.390117
6	0	-2.044980	-0.648095	-1.390117
6	0	-2.045790	0.555035	0.694854
6	0	-2.045790	0.555035	-0.694854
1	0	-2.044655	-2.790552	1.237208
1	0	-2.044655	-2.790552	-1.237208
1	0	-2.039689	-0.647279	2.475732
1	0	-2.039689	-0.647279	-2.475732
1	0	-2.043890	1.495707	1.237829
1	0	-2.043890	1.495707	-1.237829
1	0	0.826245	-0.950699	0.000000
52	0	1.576341	0.544659	0.000000
1	0	3.089510	-0.174752	0.000000

M06/BSS-F C, H : 6-311++G(d,p), O : 6-311+G(3df)
Adduct $OH_2\text{---}\pi(C_6H_6)$
Symmetry C_2
energy E = -308.5396674 au
Standard orientation

6	0	0.000000	1.389415	-0.622771
6	0	-1.203262	0.693591	-0.623454
6	0	1.203446	0.695550	-0.623546
6	0	-1.203446	-0.695550	-0.623546
6	0	1.203262	-0.693591	-0.623454
6	0	0.000000	-1.389415	-0.622771
1	0	-0.000397	2.475303	-0.625879
1	0	-2.144231	1.235853	-0.627639
1	0	2.143628	1.238347	-0.622629
1	0	-2.143628	-1.238347	-0.622629
1	0	2.144231	-1.235853	-0.627639
1	0	0.000397	-2.475303	-0.625879
1	0	0.398450	-0.642258	2.145003
8	0	0.000000	0.000000	2.737444
1	0	-0.398450	0.642258	2.145003

M06/BSS-F C, H : 6-311++G(d,p), S : 6-311+G(3df)
Adduct $SH_2\text{---}\pi(C_6H_6)$
Symmetry C_1
energy E = -631.5025888 au
Standard orientation

6	0	-1.098676	1.316839	-0.440444

6	0	-1.098773	1.039521	0.921317
6	0	-1.098664	0.277295	-1.361952
6	0	-1.098614	-0.277295	1.361967
6	0	-1.098808	-1.039521	-0.921303
6	0	-1.098662	-1.316839	0.440459
1	0	-1.101141	2.346991	-0.784478
1	0	-1.098992	1.852499	1.641275
1	0	-1.095913	0.494468	-2.425672
1	0	-1.095822	-0.494467	2.425686
1	0	-1.099056	-1.852499	-1.641261
1	0	-1.101116	-2.346991	0.784493
1	0	1.728034	-0.962576	0.000075
16	0	2.668071	-0.000002	-0.000007
1	0	1.728052	0.962590	-0.000270

M06/BSS-F C, H : 6-311++G(d,p), Se : 6-311+G(3df)
Adduct SeH_2---$\pi(C_6H_6)$
Symmetry C_2
energy E = -2634.7453355 au
Standard orientation

6	0	1.202450	0.693628	-1.758169
6	0	0.000000	1.389725	-1.757103
6	0	1.202698	-0.695699	-1.758146
6	0	-1.202698	0.695699	-1.758146
6	0	0.000000	-1.389725	-1.757103
6	0	-1.202450	-0.693628	-1.758169
1	0	2.143562	1.236097	-1.761631
1	0	0.000711	2.475440	-1.754504
1	0	2.143105	-1.238559	-1.757026
1	0	-2.143105	1.238559	-1.757026
1	0	-0.000711	-2.475440	-1.754504
1	0	-2.143562	-1.236097	-1.761631
1	0	-0.907992	-0.522150	1.073920
34	0	0.000000	0.000000	2.108221
1	0	0.907992	0.522150	1.073920

M06/BSS-F C, H : 6-311++G(d,p), Te : 74331111/7431111/74111/21
Adduct TeH_2---$\pi(C_6H_6)$
Symmetry C_2
energy E = -6847.3711044 au
Standard orientation

6	0	1.202390	-0.695238	-2.301113
6	0	1.202256	0.694057	-2.301380
6	0	0.000000	-1.389906	-2.300876
6	0	0.000000	1.389906	-2.300876
6	0	-1.202256	-0.694057	-2.301380
6	0	-1.202390	0.695238	-2.301113
1	0	2.143012	-1.237999	-2.300338
1	0	2.143325	1.236507	-2.302986
1	0	-0.000311	-2.475624	-2.297618
1	0	0.000311	2.475624	-2.297618
1	0	-2.143325	-1.236507	-2.302986

1	0	-2.143012	1.237999	-2.300338
1	0	-1.131951	-0.369073	0.658430
52	0	0.000000	0.000000	1.833182
1	0	1.131951	0.369073	0.658430