Research Article

Dynamic and Static Nature of Br₄ σ(4c–6e) and Se₂Br₅ σ(7c–10e) in the Selenanthrene System and Related Species Elucidated by QTAIM Dual Functional Analysis with QC Calculations

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The nature of Br₄ σ(4c–6e) of the Br⁺···Br···Br···Br⁻ form is elucidated for SeC₁₂H₈(Br)Se···Br—Br—Br—Br—Se(C₁₂H₈Se)Br, the selenanthrene system, and the models with QTAIM dual functional analysis (QTAIM-DFA). Asterisks (*) are employed to emphasize the existence of bond critical points on the interactions in question. Data from the fully optimized structure correspond to the static nature of interactions. In our treatment, data from the perturbed structures, around the fully optimized structure, are employed for the analysis, in addition to those from the fully optimized one, which represent the dynamic nature of interactions.

The Br⁺···Br and Br⁺···Br interactions are predicted to have the CT-TBP (trigonal bipyramidal adduct formation through charge transfer) nature and the typical hydrogen bond nature, respectively. The nature of Se₂Br₅ σ(7c–10e) is also clarified typically, employing an anionic model of [Br···Se(C₄H₄Se)···Br···Br···Br···Se(C₄H₄Se)···Br], the 1,4-diselenin system, rather than (BrSeC₁₂H₈)Br—Se—Br—Se—Br—Se(C₁₂H₈Se)—Br, the selenanthrene system.

1. Introduction

We have been much interested in the behavior of the linear interactions of the σ-type, higher than σ(3c–4e: three center-four electron interactions) [1–6], constructed by the atoms of heavier main group elements. We proposed to call such linear interactions the extended hypervalent interactions, σ(ₘc–ₙₑ: 4 ≤ ℓ; ℓ < 2m) [7–13]. The σ(4c–6e) interactions are strongly suggested to play an important role in the development of high functionalities in materials and in the key processes of biological and pharmaceutical activities, recently. The bonding is applied to a wide variety of fields, such as crystal engineering, supramolecular soft matters, and nanosciences [4, 14–23]. The linear alignments of four chalcogen atoms were first demonstrated in the naphthalene system, bis[8-(phenylchalcogenyl)naphthyl]-1,1’-dichalcogenides [E: 1-(8-Ph₃EC₁₀H₈)₆E₆(C₁₀H₈₆E₆Ph₃’)-1’ (₆E, ₆E = S and Se)] [7–12]. It was achieved through the preparation and the structural determination by the X-ray crystallographic analysis. The linear E₂···E₂···E₂ interactions in I are proposed to be analysed as the E₂E₂σ(4c–6e) model not by the double E₂E₂σ(3c–4e) model. E₂E₂σ(4c–6e) in I is characterized by the CT interaction of the nₚ(₆E) → σ*(₆E···₆E) → nₚ(₆E) form [8, 10–12], where nₚ(₆E) stands for the p-type nonbonding orbitals of₆E and σ*(₆E···₆E) are the σ* orbitals of₆E···₆E. The novel reactivity of E₂E₂σ(4c–6e) in I was also clarified [8].
E(C10H4X-8')-1 [II (E, X) = (S, Cl), (S, Br), (Se, Cl), and (Se, Br)] was similarly clarified very recently [38].

The σ(4c–6e) interaction will also be produced even if both $^8E$ and $^\Lambda E$ in $^8E_2^2E_2$ are replaced by X. X4 $\sigma$(4c–6e) should also be stabilized through CT of the $n_\sigma(X) \rightarrow \sigma(X-X) \rightarrow n_\sigma(X)$ form. The energy lowering of the system through the CT interaction must be the driving force for the formation of X4 $\sigma$(4c–6e). X4 $\sigma$(4c–6e) is the typical kind of halogen bonds, together with E2X2 $\sigma$(4c–6e), which are of current and continuous interest [39]. Br3 $\sigma$(4c–6e) has been clearly established in the selenanthrene system, SeC12H4(Br) SeBr...Br-Br...BrSe(C12H4Se) (1), through the preparation and the structural determination by the X-ray crystallographic analysis [39]. The atoms taking part in the linear interaction in question are shown in bold. The structure of (BrSeC12H4)Br...Se...Br-Br...BrSe(C12H4Se)-Br (2) was also reported, in addition to 1, which is suggested to contain Se2Br3 $\sigma$(7c–10e) since the seven atoms of Se2Br3 align almost linearly in crystals. Figure 1 shows the structures of 1 and 2 determined by the X-ray analysis and the approximate MO model for $\sigma$(4c–6e) and $\sigma$(7c–10e).

It is challenging to elucidate the nature of Br4 $\sigma$(4c–6e) of the $n_\sigma$(Br)$\rightarrow$ $\sigma$(Br-Br)$\rightarrow n_\sigma$(Br) form in 1 and Se2Br5 $\sigma$(7c–10e) in 2, together with the related species. Figure 2 illustrates the process assumed for the formation of 1 and 2 from selenanthrene (S: SeC12H4Se). In this process, (SeC12H4)Br Se-Br...Br-Se(C12H4Se)-Br (3) should be formed first in the reaction of S with Br2, and then react with Br2 to yield Br2Se(Se-C12H4Se)-Br...Br-Se...Br-Br...BrSe(C12H4Se)-Br (4). The almost linear alignment of Br=Se...Br in 4 could be analysed by the SeBr3 $\sigma$(4c–6e) model, where the Br and Se atoms in 4 are placed in close proximity in space. While containing Br4 $\sigma$(4c–6e) forms in the reaction of 3 + Br2 + 3, the reaction of 3 + 4 yields 2, consisting Se2Br5 $\sigma$(7c–10e). Both 1 and 2 are recognized as the Br2-contained species. While XC4H6(Br) SeBr...Br-Br...BrSe(Br)C12H4X (5 (X = Se) and 6 (X = S)), models of 1, also consisted of Br3 $\sigma$(4c–6e), Se2Br5 $\sigma$(7c–10e) will appear typically in the anionic species, [Br3Se(Me2)-Br...Br...Br-Se(SeMe2)-Br]− (7) and [Br2Se(C12H4)-Br...Br...Br-Se(SeC12H4Se)-Br]− (8), models of 2. Species, 5, 6, 7, and 8, are shown in Figure 2, where 5, 6, and 8 belong to the 1,4-diselenin system.

What are the differences and similarities between X4 $\sigma$(4c–6e), $E_4 \sigma$(4c–6e), and $E_2X_2 \sigma$(4c–6e)? The nature of X4 $\sigma$(4c–6e) in 1 (X = Br) is to be elucidated together with the models. Models, other than 5 and 6, are also devised to examine the stabilization sequence of Br4 $\sigma$(4c–6e). H2Br4 (C2h) and Me6Br4 (C2h) have the form of R-Br...Br-Br...Br...Br (RBrR: R = H and Me), which are called the model group A (G(A)). The electronic efficiency to stabilize Br4 $\sigma$(4c–6e) seems small for R in G(A). Br6 (C3h) is detected as the partial structure in the crystals of Br6 [40]. Br6 (C3h) in the crystals is denoted by Br6 (C3h)obsd. The optimized structure of Br6 (C3h) has one imaginary frequency, which belongs to G(A), together with Br6 (C3h)obsd. The optimized structure of Br4 retains the C2 symmetry, (Br4 (C2)), which also belongs to G(A). The CT interaction of the $n_\sigma$(Br-Br)$\rightarrow$ $\sigma$(Br-Br)$\rightarrow n_\sigma$(Br) form in Br4 $\sigma$(4c–6e) will be much stabilized if the large negative charge is developed at the $^8$Br atoms in Br-(R2)SeBr-Br...$^8$Br-Br...Br-Se(R2)-Br, where the $^7$Se$^8$Br$^8$Br$^8$Br is around 90°. The highly negatively charged $^8$Br in Br-Se(R2)-$^8$Br (R = H and Me) of $\sigma$(3c–4e) is employed to stabilize Br4 $\sigma$(4c–6e), in this case. The models form G(B). The nature of Br4 $\sigma$(4c–6e) in 5 and 6 is similarly analysed, which belongs to G(B). Br4$^{-}$ (D4h) also belongs to G(B) although one imaginary frequency was predicted for Br4$^{-}$, if optimized at the MP2 level. Figure 3 illustrates the story for the stabilization of Br4 $\sigma$(4c–6e) in the sequence of the species, starting from G(A) to 1, via G(B). Figure 3 also shows the $^8$Br-Br...$^8$Br...Br-Br...Br-R. A chemical bond or interaction between atoms A and B is denoted by A-B, which corresponds to a bond path (BP) in the quantum theory of atoms in molecules (QTAIM) approach, introduced by Bader [28–37]. We will use A>B-B for BP, where the asterisk emphasizes the existence of a bond critical point (BCP, *) in A-B [28, 29]. (Dots are usually employed to show BCPs in molecular graphs. Therefore, A>B-B would be more suitable to describe the BP with a BCP. Nevertheless, A>B-B is employed to emphasize the existence of a BCP on the BP in question in our case. BCP is a point along BP at the interatomic surface, where $\rho(r)$ (charge density) reaches a minimum along the interatomic (bond) path, while it is a maximum on the interatomic surface separating the atomic basins). The chemical bonds and interactions are usually classified by the signs of Laplacian rho ($V^2\rho_b(r_c)$) and Hb($r_c$) at BCPs, where $\rho_b(r_c)$ and Hb($r_c$) are the charge densities and total electron energy densities at BCPs, respectively (see Scheme S1 in Supplementary File). The relations between Hb($r_c$), $V^2\rho_b(r_c)$, Gb($r_c$) (the kinetic energy densities), and $V_b(r_c)$ (the potential energy densities) are represented in equations (1) and (2):

$$H_b(r_c) = G_b(r_c) + V_b(r_c),$$

$$\left(\frac{\hbar^2}{8m}\right)V^2\rho_b(r_c) = H_b(r_c) - \frac{V_b(r_c)}{2}$$

$$G_b(r_c) + \frac{V_b(r_c)}{2}.$$

How can the nature of Br4 $\sigma$(4c–6e) and Se2Br5 $\sigma$(7c–10e) be clarified? For the characterization of interactions in more detail, we recently proposed QTAIM dual functional analysis (QTAIM-DFA) [42–47] for experimental chemists to analyze their own chemical bonds and interaction results based on their own experiments, according to the QTAIM approach [28–37]. Hb($r_c$) is plotted versus $H_b(r_c) - V_b(r_c)$/$2 = (\hbar^2/8m)V^2\rho_b(r_c)$ at BCPs in QTAIM-DFA. The classification of interactions by the signs of $V^2\rho_b(r_c)$ and Hb($r_c$) is incorporated in QTAIM-DFA. Data from the fully optimized structures correspond to the static natures of the interactions, which are analysed using the polar coordinate (R, θ), representation [42, 44–46]. Each interaction plot, containing data from both the perturbed structures and the fully optimized one include a specific curve that provides important information about the interaction. This plot is expressed by (θp, $\kappa_p$), where θp...
corresponds to the tangent line of the plot and \( \kappa_p \) is the curvature. The concept of the dynamic nature of interactions has been proposed based on \((\theta_p, \kappa_p)\) [42, 44]. \( \theta \) and \( \theta_p \) are measured from the \( y \)-axis and the \( y \)-direction, respectively. We call \((R, \theta)\) and \((\theta_p, \kappa_p)\) QTAIM-DFA parameters, which are drawn in Figure 4, exemplified by \( \text{Br}_2^+ \) (\( D_{coh} \)). While \((R, \theta)\) classifies the interactions, \((\theta_p, \kappa_p)\) characterizes them.

We proposed a highly reliable method to generate the perturbed structures for QTAIM-DFA very recently [48]. The method is called CIV, which employs the coordinates derived from the compliance force constants \( C_{ij} \) for the internal vibrations. Compliance force constants \( C_{ij} \) are defined as the partial second derivatives of the potential energy due to an external force, as shown in equation (3), where \( i \) and \( j \) refer to the internal coordinates and the force constants \( f_i \) and \( f_j \) correspond to \( i \) and \( j \), respectively. The \( C_{ij} \) values and the coordinates corresponding to the values can be calculated using the compliance 3.0.2 program, released by Brandhorst and Grunenberg [49–52]. The dynamic nature of interactions based on the perturbed structures with CIV is described as the “intrinsic dynamic nature of interactions” since the coordinates are invariant to the choice of the coordinate system:

\[
C_{ij} = \frac{\partial^2 E}{\partial f_i \partial f_j} \quad (3)
\]

QTAIM-DFA has excellent potential for evaluating, classifying, characterizing, and understanding weak to strong interactions according to a unified form. The superiority of QTAIM-DFA to elucidate the nature of interactions, employing the perturbed structures generated with CIV, is explained in the previous papers [48, 53] (see also Figure S2 and Table S2 in Supplementary File). QTAIM-DFA is applied to standard interactions and rough criteria that distinguish the interaction in question from others which are obtained. QTAIM-DFA and the criteria are explained in Supplementary File using Schemes S1–S3, Figures S1 and S2, Table S1, and equations (S1)–(S7). The basic concept of the QTAIM approach is also explained.

We consider QTAIM-DFA, employing the perturbed structures generated with CIV, to be well suited to elucidate the nature of \( \text{Br}_4 \sigma(4c–6e) \) in 1, \( \text{Se}_2\text{Br}_3 \sigma(7c–10e) \) in 2, and the models derived from 1 and 2, together with the related linear interactions. The interactions in \( \text{Br}_4 \sigma(4c–6e) \) are denoted by \( \text{Br}^* \cdot \cdot \cdot \text{Br}^* \cdot \cdot \cdot \text{Br} \cdot \cdot \cdot \text{Br} \), where the asterisk emphasizes the existence of a BCP in the interactions, so are those in \( \text{Se}_2\text{Br}_3 \sigma(7c–10e) \). Herein, we present the results of the investigations on the extended hypervalent interactions in the species, together with the structural feature. Each interaction is classified and characterized, employing the criteria as a reference.

2. Methodological Details in Calculations

Calculations were performed employing the Gaussian 09 programs package [54]. The basis sets employed for the calculations were obtained, as implemented from Sapporo Basis Set Factory [55]. The basis sets of the (621/31/2), (621/621/3), (7321/7421/72), and (743211/74111/721/2+1s1p) forms were employed for C, S, Se, and Br, respectively, with the (31/3) form for H. The basis set system is called BSS-A.
All species were calculated employing BSS-A, and the Møller–Plesset second-order energy correlation (MP2) level [56–58] was applied for the optimizations. Optimized structures were confirmed by the frequency analysis. The results of the frequency analysis were used to calculate the \( C_{ij} \) values and the coordinates \( (C_i) \) corresponding to the values.

DFT level of CAM-B3LYP [59] was also applied when necessary. QTAIM functions were analysed with the AIM2000 [60] and AIMAll [61] programs.

The method to generate perturbed structures with CIV is the same as that explained in the previous papers [48, 53]. As shown in equation (4), the \( i \)-th perturbed structure in question \( (S_{nw}) \) is generated by the addition of the \( i \)-th coordinates \( (C_i) \) to the standard orientation of a fully optimized structure \( (S_o) \) in the matrix representation. The coefficient \( f_{nw} \) in equation (4) controls the structural difference between \( S_{nw} \) and \( S_o; (C_i) \) determined by the X-ray analysis are denoted by 1

\[
S_{nw} = S_o + f_{nw} \cdot C_i \tag{4}
\]

\[
r = r_o + w \alpha_o,
\]

\[
(w = (0), \pm 0.05, \text{and} \pm 0.1; \alpha_o = 0.52918 \text{ \AA}) \tag{5}
\]

\[
y = c_o + c_1x + c_2x^2 + c_3x^3,
\]

\[
(R^2: \text{square of correlation coefficient}) \tag{6}
\]

In QTAIM-DFA, \( H_b(r_c) \) is plotted versus \( H_b(r_c) - V_b(r_c)/2 \) for data of \( w = 0, \pm 0.05, \text{and} \pm 0.1 \) in equation (5). Each plot is analysed using a regression curve of the cubic function, as shown in equation (6), where \( (x, y) = (H_b(r_c) - V_b(r_c)/2 \text{ and } H_b(r_c)) \) \( \alpha \) (square of correlation coefficient) > 0.99999 in usual) [46].

3. Results and Discussion

3.1. Structural Optimizations. The structures of 1 \((C_1)\) and 2 \((C_4)\) determined by the X-ray analysis are denoted by 1
obsd and 2 (C₁)obsd, respectively [39]. The structural parameters are shown in Tables S2 and S3 in Supplementary File, respectively. Figure 3 contains the selected structural parameters for 1 (C₁)obsd. The structures are optimized for G(A) of H₂Br₄ (C₂v), Me₂Br₄ (C₂v), Br₆ (C₂v), and Br₆ (C₂) and G(B) of H₂Se₂Br₆ (C₃), Me₂Se₂Br₆ (C₁), 5 (C₆), and 6 (C₆), together with 3 (C₆), 4 (C₁), 7 (C₂h), 8 (C₂h), and Br₂ (D∞h). The optimized structural parameters are also collected in Tables S2 and S3 in Supplementary File. The frequency analysis was successful for the optimized structures, except for 1 (C₁)obsd and Br₆ (C₂). All positive frequencies were obtained for 1 (C₁), if calculated with CAM-B3LYP/BSS-A, which confirms the structure. The Br--Br distances of Br₄ σ(4c–6e) in 1 (C₁) are somewhat longer if optimized at the CAM-B3LYP level, relative to 1 (C₁)obsd. While one imaginary frequency is detected in Br₆ (C₂), Br₆ (C₂) has all positive frequencies. The optimized structures are not shown in figures, instead, some of them can be found in Figures 3 and 5, where the molecular graphs are drawn on the optimized structures. Figure 3 contains the optimized (ABr–ABr) and (ABr–BBr) distances for the models and the charge developed at BBr in the original R–Br and Br–(R₂)Se–BBr (Qₙ(BBr)), which give the models of G(A) and G(B), respectively. The (ABr–BBr) values become shorter in the order shown in equation (7), if evaluated with MP2/BSS-A:
### 3.2. Energies for Formation of $Br_4 \sigma(4c–6e)$ and NBO Analysis

Energies for the formation of $R\text{Br}_4 R'$ from the components ($2R\text{Br} + Br_4$) ($\Delta E$) are defined by equation (8). The $\Delta E$ values evaluated on the energy surface are denoted by $\Delta E_{ES}$, while those corrected with the zero-point energies are by $\Delta E_{ZP}$. The $\Delta E_{ES}$ and $\Delta E_{ZP}$ values for the optimized structures are given in Table S2 in Supplementary File. $\Delta E_{ZP}$ are excellently correlated to $\Delta E_{ES}$, ($\Delta E_{ZP} = 0.99 \Delta E_{ES} + 1.93; R^2 = 0.9998$, see Figure S3 in Supplementary File):

$$\Delta E(R' Br_4) = E(R' Br_4) - [2E(R' Br) + E( Br_4)],$$

$$E(2) = q_i \times \frac{F(i, j)^2}{(\epsilon_j - \epsilon_i)}.$$  

### 3.3. Molecular Graphs with Contour Plots for the Species Containing $Br_4 \sigma(4c–6e)$, $Se_2 Br_5 \sigma(7c–10e)$, and Related Linear Interactions

Before application of QTAIM-DFA to $Br_4 \sigma(4c–6e)$ and $Se_2 Br_5 \sigma(7c–10e)$, molecular graphs were examined, as shown in the next section.
3. Survey of $\text{Br}_4$ $\sigma(4c-6e)$ and $\text{Se}_2\text{Br}_5$ $\sigma(7c-10e)$. BPs in $\text{Br}_4$ $\sigma(4c-6e)$ and $\text{Se}_2\text{Br}_5$ $\sigma(7c-10e)$ seem straight, as shown in Figures 3 and 5. To show the linearity more clearly, the lengths of BPs ($r_{BP}$) for $\text{Br}_4$ $\sigma(4c-6e)$ are calculated. The values are collected in Table S5 in Supplementary File, together with the corresponding straight-line distances ($R_{SL}$).
The table contains the values for Se₂Br₆ σ(7c–10e) in 7 (C₂h) and 8 (C₃ᵥ). The differences between them (Δrₕₑ = rₕₑ−rₕₑ) are less than 0.003 Å. The rₕₑ values are plotted versus δₕₑ, which are shown in Figure S5 in Supplementary File. The correlations are excellent, as shown in the figure. Therefore, Br₄ σ(4c–6e) and Se₂Br₆ σ(7c–10e) in the species can be approximated by the straight lines.

QTAIM functions are calculated for Br₄ σ(4c–6e) at BCPs. Table 1 collects the values for the interactions. Hₙ(rₙ) is plotted versus Hₙ(rₙ)−Vₙ(rₙ)/2 for the data shown in Table 1, together with those from the perturbed structures generated with CIV. Figure 4 shows the plots for the ABr−*ABr and ABr−*BBr interactions in Br₄ σ(4c–6e) of the bromine species. The plots for ABr−*ABr appear in the region of Hₙ(rₙ)−Vₙ(rₙ)/2 > 0 and Hₙ(rₙ) < 0, for all species, except for the original Br₂ (Dₙₐₔₙ₈), of which the plot appears in the region of Hₙ(rₙ)−Vₙ(rₙ)/2 < 0 and Hₙ(rₙ) > 0. Therefore, the interactions are all classified by the regular-CS (closed shell) interactions, except for Br₄ (Dₙₐₔₙ₈), which is classified by the SS (shard shell) interaction. On the contrary, data of ABr−*BBr appear in the region of Hₙ(rₙ)−Vₙ(rₙ)/2 > 0 and Hₙ(rₙ) > 0 for all species, except for those in H₂Se₂Br₆ (C₇), Me₄Se₂Br₆ (C₅), H₂Br₄ (C₁), and 6 (C₆). which appear in the region of Hₙ(rₙ)−Vₙ(rₙ)/2 > 0 and Hₙ(rₙ) < 0. As a result, ABr−*BBr is classified by the pure-CS interactions (p-CS) for all, except for the four species, of which ABr−*BBr is classified by the regular-CS interactions (r-CS). The ABr−*BBr interaction in Br₂⁻ (Dₙₐₔₙ₈) is very close to the borderline between p-CS and r-CS since Hₙ(rₙ) = 0.0001 au for Br₂⁻ (Dₙₐₔₙ₈), which is very close to zero. QTAIM-DFA parameters of (R, θ) and (θₚ, κₚ) are obtained by analysing the plots of Hₙ(rₙ) versus Hₙ(rₙ)−Vₙ(rₙ)/2 in Figure 4, according to equations (3)–(6). Table 1 collects the QTAIM-DFA parameters for Br₄ σ(4c–6e). The classification of interactions will also be discussed based on the (R, θ) values.

QTAIM functions are similarly calculated for Se₂Br₆ σ(7c–10e) at BCPs, together with the related interactions. Hₙ(rₙ) is similarly plotted versus Hₙ(rₙ)−Vₙ(rₙ)/2 although not shown in the figures. Then, QTAIM-DFA parameters of (R, θ) and (θₚ, κₚ) are obtained by analysing the plots, according to equations (3)–(6). Table 2 collects the QTAIM-DFA parameters of (R, θ) and (θₚ, κₚ) for Br₄ σ(4c–6e).

3.5. Nature of Br₄ σ(4c–6e). Interactions are characterized by (R, θ), which correspond to the data from the fully optimized structures. On the contrary, they are characterized employing (θₚ, κₚ) derived from the data of the perturbed structures around the fully optimized structures and the fully optimized ones. In this case, the nature of interactions is substantially determined based of the (R, θ, θₚ) values, while the κₚ values are used only additionally. It is instructive to survey the criteria before detailed discussion. The criteria tell us that 180° < θ < 180° (rₕₑ(rₙ) < rₕₑ) for the r-CS interactions, and 45° < θ < 90° (rₕₑ(rₙ) > rₕₑ) for p-CS interactions. The θₚ value characterizes the interactions. In the p-CS region of 45° < θ < 90°, the character of interactions will be the vDW type for 45° < θ < 90°, whereas it will be the typical HB type without covalency (t-HB_{wb}) for 90° < θ < 125°, where θₚ = 125° is tentatively given for θ = 90°. The CT interaction will appear in the r-CS region of 90° < θ < 180°. The r-HB type with covalency (r-HB_{wb}) appears in the region of 125° < θ < 150° (90° < θ < 115°), where (θₚ, θ_{wb}) = (115°, 150°) is tentatively given as the borderline between t-HB_{wb} and the CT-MC nature. The borderline for the interactions between CT-MC and CT-‘TBP types is defined by θₚ = 180°. θ = 150° is tentatively given for θ = 180°. Classical chemical bonds of SS (180° < θ) will be strong (Cov-s) when R < 0.15 au, whereas they will be weak (Cov-w) for R > 0.15 au. The classification and characterization of interactions are summarized in Table S1 and Scheme S3 in Supplementary File.

The ABr−*ABr and ABr−*BBr interactions of Br₄ σ(4c–6e) will be classified and characterized based on the (R, θ, θₚ) values, employing the standard values as a reference (see Scheme S2 in Supplementary File). R < 0.15 au for all interactions in Table 1; therefore, no Cov-s were detected in this work. The (θ, θₚ) values are (180.1°, 191.8°) for the original Br₂ (Dₙₐₔₙ₈) if evaluated with MP2/BSS-A. Therefore, the nature of Br−*ABr in Br₂ (Dₙₐₔₙ₈) is classified by the SS interactions and characterized as the Cov-w nature, which is denoted by SS/Cov-w. The (θ, θₚ) values are (167.5–170°, 155.0–161°) for ABr−*ABr in the optimized structures of 6 (C₇), Br₂ (C₂₃), and R₂Br₄ (C₄₀) (R = H and Me); therefore, the nature is predicted to be r-CS/CS-TBP. The nature of ABr−*BBr in Br₂ (Dₙₐₔₙ₈) is classified as Cov-w, which is denoted by SS/Cov-w. The (θ, θₚ) values are (78.0–84.1°, 94.7–105.1°) for ABr−*BBr in the optimized structures of 6 (C₇), Br₂ (C₂₀), and R₂Br₄ (C₄₀) (R = H and Me); therefore, the nature is predicted to be r-CS/TBP. The nature of ABr−*BBr in Br₂ (Dₙₐₔₙ₈) is classified as Cov-w, which is denoted by SS/Cov-w. The (θ, θₚ) values are (90.9–92.8°, 116.4–122.5°). The characteristic nature of the E−*E−*E−*E interactions in Br₂⁻ (Dₙₐₔₙ₈) was controlled by the double negative charges in the species.

The results in Table 1 show that the ABr−*ABr interaction in Br₂ σ(4c–6e) becomes weaker, as the strength of the corresponding ABr−*BBr increases. The strength of ABr−*ABr becomes weaker in the order shown in equation (10), if evaluated by θ, while that of ABr−*BBr increases in the order shown in equation (11), if measured by θ. Very similar results were obtained by θₚ:

θ for ABr−*ABr:

\[
\begin{align*}
\text{Br}_2(D_{coh}) & > \text{H}_2\text{Br}_4(C_{2h}) > \text{Br}_6(C_2 \text{ and } C_{2h}) \\
& > \text{Me}_2\text{Br}_4(C_{2h}) > \text{H}_2\text{Se}_2\text{Br}_6(C_7) > \text{Me}_4\text{Se}_2\text{Br}_6(C_7) \\
& \geq 1(C_{obsd}) > 6(C_7) > \text{Br}_2(C_{2h, obsd}) \\
\theta & \text{ for ABr−*BBr:}
\end{align*}
\]

θ for ABr−*BBr:

\[
\begin{align*}
\text{H}_2\text{Br}_4(C_{2h}) & > \text{Br}_6(C_{2h} \text{ and } C_2) > \text{Br}_6(C_{2h, obsd}) \\
& > \text{Me}_2\text{Br}_4(C_{2h}) < 1(C_{obsd}) < \text{Me}_4\text{Se}_2\text{Br}_6(C_7) \\
& < \text{H}_2\text{Se}_2\text{Br}_6(C_7) < 6(C_7) \\
\end{align*}
\]
Table 1: QTAIM functions and QTAIM-DFA parameters for $^8$Br-$^8$Br-$^8$Br-$^8$Br at BCPs in Br$_4$ o(4c−6e), together with $^8$Br-$^8$Br in Br$_3$, evaluated with MP2/BSS-A$^3$.

| Species (symmetry) | Interaction X-$\cdots$Y | $\rho_{c}(r_{c})$ (a.u.$^{-1}$) | $\sigma^2\rho_{c}(r_{c})$ (au) | $H_{c}(r_{c})$ (au) | $k_{b}(r_{b})$ (au) | $R^b$ (au) | $\theta^b$ (°) | $\theta_{p,CIV}^b$ (°) | $\kappa_{p,CIV}^b$ (au) | Predicted nature |
|-------------------|----------------------|-------------------------------|-------------------------------|------------------|------------------|-----------|-------------|----------------|----------------|----------------|
| Br$_2$ (D$_{coh}$)$^a$ | Br-$\cdots$Br | 0.1130 | -0.0001 | -0.0497 | -2.005 | 0.0497 | 180.1 | 0.4 | 191.8 | 1.8 | SS/Cov.$^{-w}$ |
| Br$_2^b$ (D$_{coh}$)$^a$ | $^8$Br-$^8$Br | 0.0922 | 0.0052 | -0.313 | -1.751 | 0.0317 | 170.6 | 0.8 | 190.6 | 3.6 | r-CS/CT-TBP$^k$(1) |
| Br$_6$ (C$_3$) | $^8$Br-$^8$Br | 0.1099 | 0.0000 | -0.466 | -1.960 | 0.0467 | 178.8 | 0.4 | 191.3 | 2.3 | r-CS/CT-TBP$^k$(1) |
| Br$_6$ (C$_{2h}$)$^m$ | $^8$Br-$^8$Br | 0.1099 | 0.0000 | -0.466 | -1.961 | 0.0467 | 178.8 | 0.4 | 191.7 | 1.7 | r-CS/CT-TBP$^k$(1) |
| Br$_6$ (C$_{2h}$)$_{obsd}$ | $^8$Br-$^8$Br | 0.0765 | 0.0053 | -0.200 | -1.654 | 0.0207 | 165.2 | 0.8 | 191.4 | 1.8 | r-CS/CT-TBP$^k$(1) |
| Br$_6$ (C$_{2h}$)$_{obsd}$ | $^8$Br-$^8$Br | 0.0156 | 0.0055 | 0.0007 | -0.929 | 0.0055 | 82.5 | 0.8 | 191.4 | 1.8 | r-CS/CT-TBP$^k$(1) |
| H$_2$Br$_4$ (C$_{1}$) | $^8$Br-$^8$Br | 0.1011 | 0.0045 | 0.0010 | -0.881 | 0.0046 | 78.0 | 15.5 | 94.7 | 100 | p-CS/št-HBr$_{\gamma}$ |
| Me$_2$Br$_4$ | $^8$Br-$^8$Br | 0.1076 | 0.0066 | -0.444 | -1.932 | 0.0445 | 177.9 | 0.4 | 191.4 | 1.8 | r-CS/CT-TBP$k$(1) |
| H$_2$Se$_2$Br$_6$ (C$_{1}$) | $^8$Br-$^8$Br | 0.0220 | 0.0068 | -0.0002 | -1.016 | 0.0068 | 91.9 | 9.9 | 117.4 | 75 | r-CS/št-HBr$_{\gamma}$ |
| Me$_2$Se$_2$Br$_6$ (C$_{1}$) | $^8$Br-$^8$Br | 0.0212 | 0.0067 | -0.0001 | -1.008 | 0.0067 | 90.9 | 9.9 | 116.4 | 101 | r-CS/št-HBr$_{\gamma}$ |
| 5 (C$_{1}$)$^g$ | $^8$Br-$^8$Br | 0.0226 | 0.0070 | -0.0003 | -1.023 | 0.0070 | 92.7 | 6.8 | 118.0 | 557 | r-CS/št-HBr$_{\gamma}$ |
| 5 (C$_{1}$)$^g$ | $^8$Br-$^8$Br | 0.0226 | 0.0070 | -0.0003 | -1.023 | 0.0070 | 92.7 | 6.8 | 118.0 | 557 | r-CS/št-HBr$_{\gamma}$ |
| 6 (C$_{1}$) | $^8$Br-$^8$Br | 0.0147 | 0.0020 | -0.383 | -1.905 | 0.0384 | 177.0 | 0.5 | 191.3 | 2.5 | r-CS/CT-TBP$^k$(1) |
| 6 (C$_{1}$) | $^8$Br-$^8$Br | 0.0145 | 0.0048 | 0.0008 | -0.904 | 0.0048 | 80.1 | 15.9 | 97.4 | 102 | p-CS/št-HBr$_{\gamma}$ |
| 6 (C$_{1}$) | $^8$Br-$^8$Br | 0.0227 | 0.0070 | -0.0004 | -1.024 | 0.0071 | 92.8 | 42.1 | 122.5 | 2474 | r-CS/CT-TBP$^k$(1) |
| 1 (C$_{1}$)$^f$ | $^8$Br-$^8$Br | 0.0144 | 0.0020 | -0.380 | -1.901 | 0.0381 | 176.9 | 0.5 | 191.3 | 2.6 | r-CS/CT-TBP$^k$(1) |
| 1 (C$_{1}$)$^f$ | $^8$Br-$^8$Br | 0.0147 | 0.0048 | 0.0008 | -0.907 | 0.0049 | 80.3 | 16.6 | 97.8 | 103 | r-CS/št-HBr$_{\gamma}$ |
| 1 (C$_{1}$)$_{obsd}$ | $^8$Br-$^8$Br | 0.0163 | 0.0038 | -0.398 | -1.939 | 0.0398 | 178.1 | 0.5 | 191.7 | 2.3 | r-CS/št-HBr$_{\gamma}$ |
| 1 (C$_{1}$)$_{obsd}$ | $^8$Br-$^8$Br | 0.0123 | 0.0043 | 0.0010 | -0.868 | 0.0043 | 76.9 | 18.3 | 91.8 | 100 | r-CS/št-HBr$_{\gamma}$ |

$^a$See the text for BSS. $^b$With one imaginary frequency for the vibration mode of the AU symmetry. $^c$With one imaginary frequency for the vibration mode of the SGU symmetry. $^d$The regular-CS interaction of the CT-TBP nature. $^e$The pure-CS interaction of the HB nature with covalency. $^f$With one imaginary frequency for the rotational mode around the linear Br−Br interaction. $^g$See ref. [40]. $^h$The regular-CS interaction of the HB nature with covalency. $^i$With one imaginary frequency for the vibration mode of the AU symmetry. $^j$With one imaginary frequency for the vibration mode of the SGU symmetry. $^k$The regular-CS interaction of the CT-TBP nature. $^l$The pure-CS interaction of the HB nature with no covalency. $^m$With one imaginary frequency for the rotational mode around the linear Br−Br interaction. $^n$See ref. [40]. $^o$The regular-CS interaction of the HB nature with covalency. $^p$With one imaginary frequency for the vibration mode of the AU symmetry. $^q$With one imaginary frequency for the vibration mode of the SGU symmetry. $^r$With one imaginary frequency for the vibration mode of the AU symmetry. $^s$See ref. [39].
Table 2: QTAIM functions and QTAIM-DFA parameters for $^\Delta$Br-$^\Delta$Se-$^\Delta$Br-$^\Delta$Se-$^\Delta$Br-$^\Delta$Se-$^\Delta$Br at BCPs in 7 ($C_{2h}$), 8 ($C_{2h}$), and 2 ($C_{2v}$) abd, together with $^\Delta$Br-$^\Delta$Se-$^\Delta$Br in 3 ($C_{2v}$) and $^\Delta$Br-$^\Delta$Se-$^\Delta$Br-$^\Delta$Se-$^\Delta$Br in 4 ($C_{2v}$), evaluated with MP2 BSS.$^A$.

| Species (symmetry) | Interaction | $\rho_b(r_c)$ (au$^{-1}$) | $cV^2\rho_b(r_c)$ (au$^{-1/2}$) | $H_b(r_c)$ (au) | $k_b(r_c)$ (au) | $R_{d1}$ (au) | $\theta^0$ (°) | $C_b$ (Å mdyn$^{-1}$) | $\theta_{p\text{CS}^{d1}}$ (°) | $\kappa_{p\text{CS}^{d1}}$ (au$^{-1}$) | Predicted nature |
|-------------------|-------------|--------------------------|-------------------------------|-----------------|-----------------|---------------|----------------|------------------|------------------|------------------|-----------------|
| 7 ($C_{2h}$)      | $^\Delta$Se-$^\Delta$Br$^2$ | 0.0423 0.0080 | -0.0056 | -1.258 | 0.0098 | 124.8 | 6.3 | 169.9 | 55 | r-CS/CT-MC$^{(i)}$ |
|                   | $^\Delta$Se-$^\Delta$Br$^3$ | 0.0825 0.0043 | -0.0264 | -1.753 | 0.0267 | 170.7 | 1.2 | 192.2 | 2.2 | r-CS/CT-TBP$^{(i)}$ |
|                   | $^\Delta$Br-$^\Delta$Se-$^\Delta$Br$^2$ | 0.0335 0.0086 | -0.0022 | -1.115 | 0.0088 | 104.6 | 9.4 | 145.5 | 102 | r-CS/t-HB$_{\text{tr}}^{(m)}$ |
|                   | $^\Delta$Se-$^\Delta$Br$^4$ | 0.0492 0.0085 | -0.0079 | -1.318 | 0.0116 | 133.0 | 2.3 | 172.7 | 53 | r-CS/CT-MC$^{(i)}$ |
| 8 ($C_{2h}$)      | $^\Delta$Se-$^\Delta$Br$^2$ | 0.0662 0.0075 | -0.0158 | -1.511 | 0.0175 | 154.6 | 2.2 | 187.7 | 17 | r-CS/CT-TBP$^{(k)}$ |
|                   | $^\Delta$Br-$^\Delta$Se-$^\Delta$Br$^2$ | 0.0398 0.0092 | -0.0038 | -1.171 | 0.0100 | 112.5 | 4.2 | 151.5 | 54 | r-CS/t-HB$_{\text{tr}}^{(m)}$ |
| 2 ($C_{2v}$)      | $^\Delta$Se-$^\Delta$Se | 0.0219 0.0065 | -0.0005 | -1.039 | 0.0065 | 94.6 | r-CS |
|                   | $^\Delta$Se-$^\Delta$Br | 0.0576 0.0102 | -0.0113 | -1.356 | 0.0152 | 137.8 | r-CS |
|                   | $^\Delta$Br-$^\Delta$Se | 0.0952 0.0068 | -0.0337 | -1.713 | 0.0343 | 168.6 | r-CS |
|                   | $^\Delta$Se-$^\Delta$Br | 0.0183 0.0062 | 0.0005 | -0.961 | 0.0062 | 85.7 | p-CS |
|                   | $^\Delta$Br-$^\Delta$Se | 0.0818 0.0063 | -0.0271 | -1.682 | 0.0278 | 166.9 | r-CS |
| 3 ($C_{2v}$)      | $^\Delta$Se-$^\Delta$Se | 0.0737 0.0061 | -0.0214 | -1.636 | 0.0223 | 164.0 | 0.8 | 185.8 | 8.4 | r-CS/CT-TBP$^{(k)}$ |
|                   | $^\Delta$Se-$^\Delta$Br | 0.0678 0.0069 | -0.0177 | -1.562 | 0.0189 | 158.7 | 1.0 | 183.0 | 18 | r-CS/CT-TBP$^{(k)}$ |
|                   | $^\Delta$Br-$^\Delta$Se | 0.0131 0.0042 | 0.0004 | -0.945 | 0.0042 | 84.0 | 6.4 | 105.1 | 84 | p-CS/t-HB$_{\text{tr}}^{(o)}$ |
| 4 ($C_{2v}$)      | $^\Delta$Se-$^\Delta$Br | 0.0425 0.0088 | -0.0052 | -1.229 | 0.0103 | 120.6 | 4.6 | 163.2 | 63 | r-CS/CT-MC$^{(i)}$ |
|                   | $^\Delta$Br-$^\Delta$Se | 0.0933 0.0059 | -0.0321 | -1.732 | 0.0326 | 169.6 | 0.9 | 192.1 | 5.6 | r-CS/CT-TBP$^{(k)}$ |

$^a$See the text for BSS. $^b$See ref. [39]. $^c$The regular-CS interaction of the CT-MC nature. $^d$The regular-CS interaction of the CT-TBP nature. $^e$The regular-CS interaction of the CT-TBP nature. $^f$The regular-CS interaction of the CT-TBP nature. $^g$The regular-CS interaction of the HB nature with no covalency. $^h$The regular-CS interaction of the HB nature with no covalency.
The results demonstrate that Se₂Br₅ σ(7c–10e) stabilize well 7 (C₂h) and 8 (C₂h) although 1 (C₁) obsd seems not so effective. The negative charge developed at the Br atom in 3 would not be sufficient to stabilize Se₂Br₅ σ(7c–10e) in 1 (C₁) obsd relative to the case of the Br⁻ anion in 7 (C₂h) and 8 (C₂h), irrespective of the highly negatively charged Br atoms in SeBr₂ σ(3c–4e) of 3.

4. Conclusion

The intrinsic dynamic and static nature of Br₄ σ(4c–6e) is elucidated for 1 (C₁) obsd and the related species with QTAIM-DFA, employing the perturbed structures generated with CIV. The Br⁻-Br interactions in Br₄ σ(4c–6e) of the models are predicted to have the r-CS/CT-TBP nature, if optimized with MP2/BSS-A. The Br⁻-Br interactions in 1 (C₁) obsd also appears in the r-CS region. On the contrary, the Br⁻-Br interactions in Br₆ (C₂h) and Br₄ (C₂h), H₂Br₂ (C₂h), and Me₂Br₄ (C₂h) are predicted to have the p-CS/HBc nature, if evaluated with MP2/BSS-A. The Br⁻-Br interactions become stronger in the order of H₂Br₄ (C₂h) < Br₆ (C₂h) < Br₄ (C₂h) < Me₂Br₄ (C₂h). The inverse order for Br⁻-Br as a whole. The results are in accordance with the CT interaction of the n₁(4Br⁻) → σ(4Br⁻Br) → nₚ(4Br⁻) form derived from Br₄ σ(4c–6e). The decreased binding force of Br⁻-Br must be transferred to Br⁻-Br in Br₄ σ(4c–6e). Namely, it is demonstrated that Br₄ σ(4c–6e) is stabilized as the strength of Br⁻-Br in Br₄ σ(4c–6e) increases, while Br⁻-Br becomes weaker relative to that in the original Br₂ (D₂h). In this process, Br₄ σ(4c–6e) is totally stabilized. The Br⁻-Br and Br⁻-Br interactions in Br₆ (C₂h) obsd and 1 (C₁) obsd are classified by the r-CS and p-CS interactions, respectively, where the interactions in Br₆ (C₂h) obsd seem somewhat weaker than those in 1 (C₁) obsd. The Se₂Br₅ σ(7c–10e) interactions are similarly elucidated for 2 (C₁) obsd and the anionic models of 7 (C₂h) and 8 (C₂h). The Se₂Br₅ σ(7c–10e) nature is clearly established for the optimized structures of 7 (C₂h) and 8 (C₂h), rather than 2 (C₁) obsd. Extended hypervalent interactions of the σ(mn-ne: 4 ≤ m; m < n ≤ 2m) type are shown to be well analysed and evaluated with QTAIM-DFA, employing the perturbed structures generated with CIV, exemplified by Br₄ σ(4c–6e) and Se₂Br₅ σ(7c–10e).

Data Availability

The data used to support the findings of this study are available in the supplementary information files.

Conflicts of Interest

The authors declare that there are no conflicts of interest regarding the publication of this paper.
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Supplementary Materials
Scheme S1: classification of interactions by the signs of $\nabla \rho_p(\mathbf{r})$ and $H_0(\mathbf{r})_p$, together with $G_p(\mathbf{r})$ and $V_p(\mathbf{r})$. Scheme S2: QTAIM-DFA: a plot of $H_0(\mathbf{r})_p$ versus $H_0(\mathbf{r})_p - V_p(\mathbf{r})_p/2$ for weak to strong interactions. Scheme S3: rough classification and characterization of interactions by $\theta$ and $\theta_\rho$, together with $h_0(\mathbf{r})_p = V_p(\mathbf{r})_p/G_p(\mathbf{r})$. QTAIM-DFA approach, computational data (Tables S2–S5 and Figures S3–S5), computation information and geometries of compounds, and graphical abstract. Figure S1: polar $(R, \theta)$ coordinate representation of $H_0(\mathbf{r})_p$ versus $H_0(\mathbf{r})_p - V_p(\mathbf{r})_p/2$, with $(\theta_\rho, \kappa_\rho)$ parameters. Figure S2: plot of $H_0(\mathbf{r})_p$ versus $\omega$ in $r^2(\nabla^2-Cl-Cl) = r_0(\nabla^2-Cl-Cl) + \omega_0$ for ‘$\nabla^2-Cl-Cl$’ (a) with the magnified picture of (a) (b) and that of $H_0(\mathbf{r})_p - V_p(\mathbf{r})_p/2$ versus $\omega$ (c). Typical hydrogen bonds without covalency and typical hydrogen bonds with covalency are abbreviated as t-HB without cov. and t-HB with cov., respectively, whereas Cov-w and Cov-s stand for weak covalent bonds and strong covalent bonds, respectively. Table S1: proposed definitions for the classification and characterization of interactions. (Supplementary Materials)

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