Intrinsic dynamic and static nature of halogen bonding in neutral polybromine clusters with the structural feature, elucidated by QTAIM dual functional analysis and MO calculations

Satoko Hayashi *, Taro Nishide, Eiichiro Tanaka and Waro Nakanishi *

1 Faculty of Systems Engineering, Wakayama University, 930 Sakaedani, Wakayama 640-8510, Japan; hayashi3@sys.wakayama-u.ac.jp and nakanisi@sys.wakayama-u.ac.jp.
* Correspondence: nakanisi@sys.wakayama-u.ac.jp; Tel.: +81-73-457-8252

Abstract: The intrinsic dynamic and static nature of the non-covalent Br-•-Br interactions in the neutral polybromine clusters is elucidated for Br4–Br12, applying QTAIM dual functional analysis (QTAIM-DFA). The asterisk (*) emphasizes the existence of the bond critical point (BCP) on the interaction in question. Data from the fully optimized structures correspond to the static nature of interactions. The intrinsic dynamic nature is originated from those of the perturbed structures generated using the coordinates derived from the compliance constants for the interactions and the fully optimized structures. The non-covalent Br-•-Br interactions in the L-shaped clusters of the Cs symmetry are predicted to have the typical hydrogen bond nature without covalency, although the first ones in the sequences have the vdW nature. The L-shaped clusters are stabilized by the n(Br)→σ*(Br–Br) interactions. The compliance constants for the corresponding non-covalent interactions are strongly correlated to the E(2) values based on NBO. Indeed, the MO energies seem not contribute to stabilize Br4 (C2h) and Br4 (D2d), but the core potentials stabilize them, relative to the case of 2Br2, maybe due to the reduced nuclear-electron distances in the average for the dimmers.

Keywords: ab initio calculations; quantum theory of atoms-in-molecules (QTAIM); bromide; structures.

1. Introduction

Halogen bonding is of current and continuous interest [1,2]. A lot of information has been accumulated relevant to the halogen bonding so far [3]. The halogen bonding is discussed on the basis of the shorter distances between halogen and other atoms in crystals [4–6]. The short halogen contacts are found in two types, the symmetric (type I) and bent (type II) geometries. The bonding is investigated also in the liquid [7,8] and gas [9] phases. The nature of the halogen bonding has been discussed based on the theoretical background, containing the molecular orbital description for the bonding and the σ-hole developed on the halogen atoms, together with the stability with the structural aspects [10]. We also reported the dynamic and static nature of the Y–X---π(C6H6) interactions, recently [11]. Halogen bonding is applied to wide variety of field in chemical and biological sciences, such as crystal engineering, supramolecular soft matters and nanoparticles. Efforts have made to unify and categorize the accumulated results and to establish the concept of the halogen bonding [3,12–15].

Structures of halogen molecules (X2) were reported, determined by the X-ray crystallographic analysis for X = Cl, Br and I [16–18]. The behavior of the bromine–bromine interactions were reported for the optimized structures of Br2–Br3 in the neutral and/or charged forms, together with Brn, so far [19,20]. Figure 1 draws the observed structure of Br2, for example. The bromine molecules seem to exist as the zig-zag structure in the infinite chains in crystals. One would find the linear alignment of three Br atoms in a L-shaped dimer ((Br2)2; Br4) and the linear alignment of four Br atoms in a double...
L-shaped trimer ((Br$_3$)$_2$; Br$_4$) in a planar Br$_2$ layer, in addition to Br$_2$ itself. The linear four Br atoms are located in the two L-shaped dimers of Br$_6$, overlapped at the central Br$_2$. While the L-shaped dimers seem to construct the zig-zag type infinite chains, the linear four Br atoms do the linear infinite chains. The attractive $n_d$(Br)$\rightarrow\sigma^*(Br\cdots Br)$ $\sigma(3c\cdots 4e)$ (three center–four electron interaction of the \(\sigma\)-type) and $n_d$(Br)$\rightarrow\sigma^*(Br\cdots Br)$ $\leftrightarrow n_d$(Br) $\sigma(4c\cdots 6e)$ must play a very important role to stabilize the Br$_4$ and Br$_6$, respectively, where $n_d$(Br) stands for the \(p\)-type non-bonding orbital of Br in the plane, perpendicular to the molecular Br$_2$ axis, and $\sigma^*(Br\cdots Br)$ is the $\sigma^*$-orbital of Br$_2$. The crystal structures of Cl$_2$ and I$_2$ are very similar to that of Br$_2$.

We have been much interested in the behavior of the halogen bonding in the polyhalogen clusters, together with the structures. How can the interactions in the polyhalogen clusters be clarified? We proposed QTAIM dual functional analysis (QTAIM-DFA) [21–25], based on the quantum theory of atoms in molecules (QTAIM) approach introduced by Bader [26,27]. In QTAIM-DFA, $H_0(r)$ are plotted versus $H_0(r) - V_0(r)/2$ ($= (\hbar^2/8m)V^2\rho_b(r)$; see Equation (SA2) in the Supplementary Materials), where $\rho_b(r)$, $H_0(r)$, and $V_0(r)$ stand for the charge densities, the total electron energy densities, and potential energy densities, respectively, at a bond critical points (BCPs, \*) on the bond paths (BPs) in this paper [26]. The kinetic energy densities at BCPs will be similarly denoted by $G_0(r)$ [26]. In our treatment, data from the fully optimized structures are plotted, together with those from the perturbed structures around the fully optimized ones. The static nature of the interactions corresponds to the data from the fully optimized structures, which are analyzed using the polar coordinate \((r, \theta)\) representation [21–25]. On the other hand, the dynamic nature originates based on the data from both the perturbed and fully optimized structures [21–25]. The plot is expressed by \((\theta_b, \kappa_b)\), where $\theta_b$ corresponds to the tangent line and $\kappa_b$ is the curvature of the plot. $\theta$ and $\theta_b$ are measured from the $y$-axis and the $y$-direction, respectively. We call \((r, \theta)\) and \((\theta_b, \kappa_b)\) the QTAIM-DFA parameters. (See also Figure 5 for the definition of \((r, \theta)\) and \((\theta_b, \kappa_b)\), illustrated exemplified by the \(r_9\) in Br$_{10}$ (C$_2$L$_5$).)

The perturbed structures necessary for QTAIM-DFA can be generated variously. Among them, a method, employing the coordinates corresponding to the compliance constants $C_{ii}$ for the internal vibrations, is shown to be highly reliable to generate the perturbed structures. The method, which we proposed recently, is called CIV [28–33]. 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 coordinate system. Rough criteria that distinguish the interaction in question from others are obtained by applying QTAIM-DFA with CIV to standard interactions. QTAIM-DFA and the criteria are explained in the Appendix of the Supplementary Materials using Schemes SA1–SA3, Figures SA1 and SA2, Table SA1, and Equations (SA1)–(SA7). The basic concept of the QTAIM approach is also explained.

QTAIM-DFA using the perturbed structures generated with CIV is well-suited to elucidate the intrinsic dynamic and static nature of the halogen-halogen interactions in the polyhalogen clusters. As the first step to clarify the nature of various types of the halogen-halogen interactions in the polyhalogen clusters, the nature of each bromine-bromine interaction in the neutral polybromine clusters is elucidated by applying QTAIM-DFA. Various types of the structures and the interactions...
are found in the optimized structures of polybromine clusters, other than those observed in the crystals. Here, we present the results of investigations on the polybromine clusters, together with the structural feature, elucidated with QTAIM-DFA and QC calculations.

2. Methodological details in calculations

Structures were optimized employing the Gaussian 09 programs [34]. The 6-311+G(3df) basis [35–38] set was applied to optimize the structures of neutral polybromine clusters, Br₃–Br₁₂. The Møller-Plesset second order energy correlation (MP2) level [39–41] was applied for the optimizations. Optimized structures were confirmed by the frequency analysis. The results of the frequency analyses were employed to calculate the Cₖ values and coordinates corresponding to Cₖ [28,30]. QTAIM functions were calculated using the Gaussian 09 program package [34] with the same method to the optimizations. Data were analyzed with the AIM2000 [42] and AIMAll [43] programs.

Coordinates corresponding to the compliance constants for an internal coordinate i of the internal vibrations (C) were employed to generate the perturbed structures, necessary in QTAIM-DFA [21–25]. Equation (1) explains the method to generate the perturbed structures with CIV. A i-th perturbed structure in question (Sᵦᵦ) was generated by the addition of the coordinates (C) corresponding to Cᵦ to the standard orientation of a fully-optimized structure (Sᵦ), in the matrix representation. The coefficient gᵦ in Equation (1) controls the difference in structures between Sᵦᵦ and Sᵦ. gᵦ are determined to satisfy Equation (2) for an interaction in question, where r and rₒ show the distances in question in the perturbed and fully optimized structures, respectively, with aₒ of Bohr radius (0.52918 Å) [21–25,28].

\[ Sᵦᵦ = Sᵦ + gᵦ • C \]  
\[ r = rₒ + wₐₒ \]  
\[ y = cₒ + c₁x + c₂x² + c₃x³ \]  
\[ (w = (0), ±0.05 and ±0.1; aₒ = 0.52918 Å) \]  
\[ (Rᵦ²: \text{square of correlation coefficient}) \]  
\[ (3) \]

In the QTAIM-DFA treatment, \( Hₒ(r) \) are plotted versus \( Hₒ(r) – Vₒ(r)/2 \) for data of five points of \( w = 0, ±0.05 \) and \( ±0.1 \) in Equation (2). Each plot is analyzed using a regression curve of the cubic function as shown in Equation (3), where \( (x, y) = (Hₒ(r) – Vₒ(r)/2, Hₒ(r)) \) \( (Rᵦ²: \text{square of correlation coefficient}) > 0.99999 \) in usual) [25].

3. Results and Discussion

3.1. Structural optimizations of polybromine clusters, Brᵦᵦ–Br₁₂

Structures of the neutral Br₃–Br₁₂ clusters were optimized with MP2/6-311+G(3df). The structural parameters for the optimized structures of minima for Br₃–Br₆ and Br₇–Br₁₂ are collected in Tables S1 and S2, respectively, of the Supplementary Materials. Table 2 contains some transition states (TSs) for Br₃ and Br₄. The notation of Cᵦ-Lₐ (m = 1–5) is used for the linear L-shaped clusters of the Cᵦ symmetry, where m stands for the number of the non-covalent interactions in Br₃m (= m = 1–5). Cyclic structures are also optimized retaining the higher symmetries. The optimized structures are not shown in figures but they can be found in the molecular graphs with the contour maps of \( \rho(r) \), drawn on the optimized structures with MP2/6-311+G(3df). (See Figure 3 for Br₄–Br₁₂ of the L-shaped clusters in the Cᵦ symmetry, Br₃(Cᵦ-Lₐ)–Br₁₂(Cᵦ-Lₐ) with Br₃(Cᵦ-Lₐ) and Figure 4 for Br₄–Br₁₂ of minima other than Cᵦ-Lₐ (m = 1–5)). The energies for the formation of Br₃–Br₆ and Br₇–Br₁₂, are given in Tables S1 and S2 of the Supplementary Materials, respectively, from the components \( (\Delta E = E(Br₃) – kE(Br₃)) \) on the energy surfaces (\( \Delta Eᵦ \)) and those with the collections of the zero-point energies (\( \Delta Eᵦr \)). The \( \Delta Eᵦ r \) values were plotted versus \( \Delta Eᵦ \). The plot is shown in Figure S1 of the Supplementary Materials, which gives an excellent correlation \( (y = 0.940x + 0.129; Rᵦ² (\text{square of correlation coefficient}) = 0.9999, \text{see also entry 1 in Table 3}) \). Therefore, the \( \Delta Eᵦ r \) values are employed for the discussion.

The behavior of the neutral di-bromine clusters (Br₃) is discussed, first. Three structures were optimized for Br₄ as minima with some TSs. The minima are the L-shaped structure of the Cᵦ
symmetry (Br$_4$ (C$_{v}$-L$_1$)) [19], cyclic structure of the C$_{3v}$ symmetry (Br$_4$ (C$_{3v}$)), and the tetrahedral type of the D$_{2h}$ symmetry (Br$_4$ (D$_{2h}$)). A TS of the C$_{v}$ symmetry was detected between Br$_3$ (C$_{v}$-L$_1$) and Br$_4$ (C$_{3v}$) and two TSs of the C$_{3v}$ symmetry were between Br$_3$ (C$_{3v}$) and Br$_4$ (D$_{2h}$) and between Br$_3$ (D$_{2h}$) and Br$_4$ (C$_{v}$-L$_1$). They are called TS (C$_v$: C$_v$, C$_{3v}$), TS (C$_v$: C$_{2v}$, D$_{2h}$), and TS (C$_v$: D$_{2h}$, C$_{3v}$), respectively. The three minima will be converted to each other through the tree TSs. A TS between Br$_3$ (C$_{v}$-L$_1$) and its topological isomer was also detected, which is called TS (C$_v$: C$_v$, C$_v$), however, further effort was not made to search similar TSs between Br$_3$ (C$_{3v}$) and its topological isomer and between Br$_4$ (C$_{3v}$) and the topological isomer.

Figure 2 draws the energy profiles for the optimized structures of minima, Br$_3$ (C$_{v}$-L$_1$), Br$_4$ (C$_{3v}$), and Br$_4$ (D$_{2h}$), together with the TSs, TS (C$_v$: C$_v$, C$_{3v}$), TS (C$_v$: C$_{2v}$, D$_{2h}$), TS (C$_v$: C$_{2v}$, C$_v$) and TS (C$_v$: C$_v$, C$_v$). The optimized structures are not shown in figures but they can be found in the molecular graphs shown in Figure 2, illustrated on the optimized structures. All BCPs expected are detected clearly, together with RCPs and a CCP [26]. The $\Delta E_{ES}$ value of –10.7 kJ mol$^{-1}$ for the formation of Br$_4$ (C$_{v}$-L$_1$) seems very close to the border area between the vdW and typical hydrogen bond (t-HB) adducts. The driving force for the formation of Br$_4$ (C$_{v}$-L$_1$) must be Br$_3$ $\sigma$(3c–4e) of the n$_{(m)}$(Br)$\rightarrow\sigma^*(Br-Br)$ type. The interactions in Br$_4$ (C$_{3v}$) and Br$_4$ (D$_{2h}$) seem very different from that in Br$_4$ (C$_{v}$-L$_1$). The $\Delta E_{ES}$ values of Br$_4$ (C$_{3v}$) (–8.0 kJ mol$^{-1}$) and Br$_4$ (D$_{2h}$) (–9.1 kJ mol$^{-1}$) are close to that for Br$_4$ (C$_{v}$-L$_1$) (–10.7 kJ mol$^{-1}$). Moreover, the values for TS (C$_v$: C$_v$, C$_{3v}$) (–7.4 kJ mol$^{-1}$), TS (C$_v$: C$_{2v}$, D$_{2h}$) (–7.6 kJ mol$^{-1}$), TS (C$_v$: D$_{2h}$, C$_v$) (–7.0 kJ mol$^{-1}$), and TS (C$_v$: C$_v$, C$_v$) (–8.7 kJ mol$^{-1}$) are not so different from those for the minima.

In the case of Br$_4$, three structures of the linear C$_{3v}$-symmetry (Br$_6$ (C$_{3v}$-L$_2$)), the linear C$_2$-symmetry (Br$_6$ (C$_2$)) and the cyclic C$_{2v}$-symmetry (Br$_6$ (C$_{2v}$-c)) were optimized typically as minima. The linear Br$_4$-clusters of the C$_{3v}$-symmetry (Br$_4$ (C$_{3v}$)) and the C$_2$-symmetry (Br$_4$ (C$_2$)), similar to Br$_6$ (C$_2$), were also optimized, of which the torsional angles, $\phi$ (Br$^2$Br$^4$Br$^4$Br$^2$) ($= \phi_1$), were 0° and 180°, respectively. One imaginary frequency was detected for each, therefore, they are assigned to TSs between Br$_4$ (C$_2$) and the topological isomer on the different reaction coordinates. Further effort was not made to search TSs.

![Figure 2. Energy profile with molecular graphs for the structures of Br$_4$ clusters, optimized with MP2/6-311+G(3df).](image)

The $\Delta E_{ES}$ value for Br$_4$ (C$_{v}$-L$_2$) was predicted to be –22.6 kJ mol$^{-1}$. The magnitude is slightly larger than the twice value for Br$_4$ (C$_{v}$-L$_1$) ($\Delta E_{ES} = –10.7$ kJ mol$^{-1}$). Two types of $\sigma$(3c–4e) operate to stabilize Br$_4$ (C$_{v}$-L$_2$). One $\sigma$(3c–4e) seems similar to that in Br$_4$ (C$_{v}$-L$_1$) but another would be somewhat different. Namely, the second interaction would contribute to $\Delta E_{ES}$ somewhat larger than that of the first one in the formation of Br$_4$ (C$_{v}$-L$_2$). On the other hand, the linear interaction in Br$_6$ (C$_2$) can be explained
by $\sigma(4c-6e)$ of the $n_2(\text{Br}) \rightarrow \sigma^*(\text{Br}-\text{Br})$ type. The magnitude of $\Delta E_{ES}$ of the $n_2(\text{C}_2)$ type is very close to the twice value for $\text{Br}_4(\text{C}_2)$-type. The magnitude of $\Delta E_{ES}$ for $\text{Br}_6(\text{C}_3)$ is close to the triplicate value of $\text{Br}_4(\text{C}_2)$-type. One finds triply degenerated $\sigma(3c-4e)$ interactions in $\text{Br}_6(\text{C}_3)$-type. The similarity in the interactions for $\text{Br}_4(\text{C}_2)$-type and $\text{Br}_6(\text{C}_3)$-type will be discussed later, again (cf: Tables 1 and 2). The magnitudes of $\Delta E_{ES}$ become larger proportionally to the size of the clusters, as shown in Figures S1 and S2 of the Supplementary Materials. The $\Delta E_{ES}$ values are plotted versus $k$ in $\text{Br}_2^k$ ($2 \leq k \leq 6$) for the $\text{C}_2$-type. The results are shown in Figure S2 of the Supplementary Materials. Contributions from inner $\sigma$($3c-4e$) (named $r_1$, $r_2$, and $r_3$, respectively) to $\Delta E_{ES}$ seems slightly larger than those from $\sigma$($3c-4e$) in the front end and end positions.

After examination of the optimized structures, next extension is to clarify the nature of the Br-Br interactions by applying QTAIM-DFA. The contour plots are discussed, next.

3.2. Molecular graphs with contour plots of polybromine clusters

Figure 3 illustrates the molecular graphs with the contour maps of $\rho(r)$ for the linear type of $\text{Br}_4(\text{C}_2)$-$\text{Br}_{12}(\text{C}_5)$, drawn on the structures optimized with MP2/6-311+G(3df). Figure 4 draws the molecular graphs with the contour maps of $\rho(r)$ for $\text{Br}_4$-$\text{Br}_{12}$, other than those for $\text{Br}_4(\text{C}_2)$-$\text{Br}_{12}(\text{C}_5)$, calculated with MP2/6-311+G(3df) [44] (see also Figure S3 of the Supplementary Materials). All BCPs expected are detected clearly, together with RCPs and a CCP, containing those for the non-covalent Br-Br interactions, which are located at the (three dimensional) saddle points of $\rho(r)$. All BCPs seem to exist inside of the molecular surfaces of the clusters, except for some, such as those on

![Figure 3](https://example.com/figure3.png)

**Figure 3.** Molecular graphs with contour plots of $\rho(r)$ for the linear type bromine clusters of $\text{Br}_4$-$\text{Br}_{12}$, calculated with MP2/6-311+G(3df). (a)-(e) for the linear $\text{C}_2$-type, (f) and (g) for the $\text{C}_2$ type, and (h) for the notations of the atoms, bonds, and angles, exemplified by $\text{Br}_{12}(\text{C}_5)$. BCPs are denoted by red dots and BPs (bond paths) are by pink lines. Bromine atoms are in reddish brown.
Figure 4. Molecular graphs with contour plots of $\rho(r)$ for the cyclic bromine clusters of Br$_4$–Br$_{12}$, (a)–(g), calculated with MP2/6-311+G(3df). BCPs are denoted by red dots, RCPs (ring-critical points) by yellow dots, CCPs (cage-critical points) by blue dots, and BPs (bond paths) are by pink lines. See ref. [45] for (a).

the non-covalent interactions of Br$_4$ ($D_2d$), Br$_4$ ($C_{2h}$) and Br$_8$ ($S_4$-Wm), although they are very near to the surfaces.

3.3. Survey of the Br-•-Br interactions in polybromine clusters

As shown in Figures 2–4, BPs in Br$_4$–Br$_{12}$ seem almost straight. The linearity is confirmed by comparing the lengths of BPs ($r_{BP}$) with the corresponding straight-line distances ($R_{SL}$). The $r_{BP}$ and $R_{SL}$ values are collected in Table S3 of the Supplementary Materials, together with the differences between them, $\Delta r_{BP} (= r_{BP} – R_{SL})$. The magnitudes of $\Delta r_{BP}$ are less than 0.01 Å, except for $r_2$ in Br$_4$ ($C_{2v}$) ($\Delta r_{BP} = 0.014$ Å), $r_3$ in Br$_8$ ($S_4$-Wm) (0.014 Å) and $r_2$ in Br$_{10}$ ($C_2$-c) (0.012 Å). Consequently, all BPs in Br$_4$–Br$_{12}$ can be approximated as the straight lines.

QTAIM functions are calculated for the Br-•-Br interactions at BCPs in the structures of Br$_2$–Br$_{12}$, optimized with MP2/6-311+G(3df) [44,45]. Table 1 collects the values for the non-covalent Br-•-Br interactions in Br$_4$–Br$_{12}$ of the $C_s$-L$_1$ type. Table 2 summarizes the values for the non-covalent Br-•-Br interactions in Br$_4$–Br$_{12}$, other than those of the $C_s$-L$_1$ type. $H_0(r_c)$ are plotted versus $H_0(r_c) – V_s(r_c)/2$ for the data shown in Tables 1 and 2, together with those from the perturbed structures generated with CIV. Figure 5 shows the plots for the non-covalent Br-•-Br interactions and covalent Br-•-Br bonds, exemplified by Br$_{10}$ ($C_2$-L$_4$).

QTAIM-DFA parameters of ($R$, $\theta$) and ($\theta_b$, $\kappa_b$) are obtained by analysing the plots of $H_0(r_c)$ versus $H_0(r_c) – V_s(r_c)/2$, according to Equations (S3)–(S6) of the Supplementary Materials. Table 1 collects the QTAIM-DFA parameters for the non-covalent Br-•-Br interactions of Br$_4$ ($C_s$-L$_1$)–Br$_{12}$ ($C_s$-L$_5$), Br$_6$ ($C_2$) and Br$_{10}$ ($C_2$), together with the $C_i$ values. Table 2 collects the ($R$, $\theta$) and ($\theta_b$, $\kappa_b$) values for Br$_4$–Br$_{12}$ other than those given in Table 1, together with the $C_i$ values. The ($R$, $\theta$) and ($\theta_b$, $\kappa_b$) values for the covalent Br-•-Br bonds in Br$_4$–Br$_{12}$ are collected in Table S4 of the Supplementary Materials.

3.4. The nature of Br-•-Br interactions in polybromine clusters

The nature of the covalent and non-covalent Br-•-Br interactions in Br$_2$–Br$_{12}$ is discussed on the basis of the ($R$, $\theta$, $\theta_b$) values, employing the standard values as a reference (see Scheme SA3 of the Supplementary Materials).
The interactions in minima are shown.

\begin{align*}
\text{Br}_2 (C-L_1) & \quad r_2 \quad 0.0109 \quad 0.0045 \quad 0.0014 \quad 0.0048 \quad 72.5 \\
\text{Br}_2 (C-L_2) & \quad r_2 \quad 0.0113 \quad 0.0047 \quad 0.0014 \quad 0.0049 \quad 73.0 \\
\text{Br}_2 (C-L_3) & \quad r_2 \quad 0.0119 \quad 0.0049 \quad 0.0014 \quad 0.0051 \quad 73.7 \\
\text{Br}_2 (C-L_4) & \quad r_2 \quad 0.0114 \quad 0.0047 \quad 0.0014 \quad 0.0049 \quad 73.2 \\
\text{Br}_2 (C-L_5) & \quad r_2 \quad 0.0124 \quad 0.0050 \quad 0.0014 \quad 0.0052 \quad 74.4 \\
\text{Br}_2 (C-L_6) & \quad r_2 \quad 0.0120 \quad 0.0049 \quad 0.0014 \quad 0.0051 \quad 73.9 \\
\text{Br}_2 (C-L_7) & \quad r_2 \quad 0.0114 \quad 0.0047 \quad 0.0014 \quad 0.0049 \quad 73.2 \\
\text{Br}_2 (C-L_8) & \quad r_2 \quad 0.0125 \quad 0.0051 \quad 0.0014 \quad 0.0053 \quad 74.6 \\
\text{Br}_2 (C-L_9) & \quad r_2 \quad 0.0125 \quad 0.0051 \quad 0.0014 \quad 0.0053 \quad 74.6 \\
\text{Br}_2 (C-L_{10}) & \quad r_2 \quad 0.0120 \quad 0.0049 \quad 0.0014 \quad 0.0051 \quad 73.9 \\
\text{Br}_2 (C-L_{11}) & \quad r_2 \quad 0.0114 \quad 0.0047 \quad 0.0014 \quad 0.0049 \quad 73.2 \\
\text{Br}_2 (C-L_{12}) & \quad r_2 \quad 0.0126 \quad 0.0051 \quad 0.0014 \quad 0.0053 \quad 74.7 \\
\text{Br}_2 (C-L_{13}) & \quad r_2 \quad 0.0127 \quad 0.0051 \quad 0.0014 \quad 0.0053 \quad 74.7 \\
\text{Br}_2 (C-L_{14}) & \quad r_2 \quad 0.0126 \quad 0.0051 \quad 0.0014 \quad 0.0053 \quad 74.7 \\
\text{Br}_2 (C-L_{15}) & \quad r_{10} \quad 0.0120 \quad 0.0049 \quad 0.0014 \quad 0.0051 \quad 73.9 \\
\text{Br}_2 (C_2) & \quad r_2 \quad 0.0104 \quad 0.0044 \quad 0.0014 \quad 0.0046 \quad 72.1 \\
\text{Br}_2 (C_2) & \quad r_2 \quad 0.0118 \quad 0.0048 \quad 0.0014 \quad 0.0050 \quad 73.6 \\
\text{Br}_2 (C_2) & \quad r_4 \quad 0.0106 \quad 0.0044 \quad 0.0014 \quad 0.0046 \quad 72.3
\end{align*}

1 The interactions in minima are shown. $^2$ $cV^2\rho(r) = H_s(r) - V_s(r)/2$ where $c = \hbar^2/8m$. $^3 R = [(H_s(r) - V_s(r)/2)^2 + H_s(r)^2]^{1/2}$. $^4 \theta = 90^\circ - \tan^{-1}[H_s(r)/(H_s(r) - V_s(r)/2)]$. $^5$ Defined in Equation (R1) in the text. $^6 \omega_\alpha = 90^\circ - \tan^{-1}(dy/dx)$, where $(x, y) = (H_s(r) - V_s(r)/2, H_s(r))$. $^7 \kappa_\alpha = |d^2y/dx^2|/[1 + (dy/dx)^2]^{3/2}$. $^8$ The pure CS interaction of the vdW nature. $^9$ The pure CS interaction of the HB nature without covalency.

### Table 1. Cont.

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<th>Species (Symmetry)</th>
<th>C^\circ (\text{Å mdyn}^{-1})</th>
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<th>$\kappa_{CB}^\circ$ (au)</th>
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<tr>
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Table 2 QTAIM functions and QTAIM-DFA parameters for Br–*–Br at BCPs in Br–Br<sub>12</sub>, other than the C<sub>r</sub>-Li<sub>r</sub> structures, evaluated with MP2/6-311+G(3df).<sup>1</sup>

<table>
<thead>
<tr>
<th>Species</th>
<th>BCP on</th>
<th>(\rho(r)) (au)</th>
<th>(cV^2\rho(r)^2) (au)</th>
<th>(H_0(r)) (au)</th>
<th>(R^3) (au)</th>
<th>(\theta^4) (°)</th>
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</thead>
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<td>Br&lt;sub&gt;r&lt;/sub&gt; (C&lt;sub&gt;r&lt;/sub&gt;)</td>
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<td>r&lt;sub&gt;2&lt;/sub&gt;</td>
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<td>0.0017</td>
<td>0.0007</td>
<td>0.0018</td>
<td>66.0</td>
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<td>0.0038</td>
<td>0.0013</td>
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<td>70.7</td>
</tr>
<tr>
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<td>0.0051</td>
<td>0.0014</td>
<td>0.0053</td>
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<td>0.0007</td>
<td>0.0016</td>
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<td>0.0040</td>
<td>0.0014</td>
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<td>0.0008</td>
<td>0.0020</td>
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<td>0.0052</td>
<td>0.0014</td>
<td>0.0054</td>
<td>75.0</td>
</tr>
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</table>

<sup>1</sup> The interactions in minima are shown.  <sup>2</sup> \(cV^2\rho(r) = H_0(r) - V_s(r)/2\) where \(c = k^2/8\pi m\).  <sup>3</sup> \(R = [(H_0(r) - V_s(r)/2)^2 + H_0(r)^2]^{1/2}\).  <sup>4</sup> \(\theta = 90° - \tan^{-1}[H_0(r)/(H_0(r) - V_s(r)/2)].\)  <sup>5</sup> Image from windmill.

Table 2. Cont.

<table>
<thead>
<tr>
<th>Species</th>
<th>C&lt;sub&gt;r&lt;/sub&gt; (Å mdyn&lt;sup&gt;-1&lt;/sup&gt;)</th>
<th>(\theta_{c-r}) (°)</th>
<th>(\kappa_{p-c}) (au&lt;sup&gt;3&lt;/sup&gt;)</th>
<th>Predicted nature</th>
</tr>
</thead>
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<tr>
<td>Br&lt;sub&gt;r&lt;/sub&gt; (C&lt;sub&gt;r&lt;/sub&gt;)</td>
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<td>122.9</td>
<td>p-CS/vdW&lt;sup&gt;9&lt;/sup&gt;</td>
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<td>40.402</td>
<td>69.6</td>
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<td>p-CS/vdW&lt;sup&gt;9&lt;/sup&gt;</td>
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<td>Br&lt;sub&gt;r&lt;/sub&gt; (C&lt;sub&gt;∞v&lt;/sub&gt;-c)</td>
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<td>71.5</td>
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<td>93.7</td>
<td>137.3</td>
<td>p-CS/t-HB&lt;sup&gt;10&lt;/sup&gt;</td>
</tr>
</tbody>
</table>

<sup>5</sup> Image from windmill.  <sup>6</sup> Defined in Equation (R1) in the text.  <sup>7</sup> \(\theta_t = 90° - \tan^{-1}(dy/dz), \) where \((x, y, z) = (H_0(r) - V_s(r)/2, H_0(r)).\)  <sup>8</sup> \(\kappa_p = 1|dz^2/dx^2|/[1 + (dy/dz)^2]^{1/2}.\)  <sup>9</sup> The pure CS interaction of the vdW nature.  <sup>10</sup> The pure CS interaction of the HB nature without covalency.

Figure 5. QTAIM-DFA plots \((H_0(r)\) versus \(H_0(r) - V_s(r)/2\) for the interactions in Br<sub>r</sub> (C<sub>r</sub>-Li) evaluated with MP2/6-311+G(3df). Marks and colors are shown in the figure.
It must be instructive to survey the criteria shown in Scheme SA3 of the Supplementary Materials, before detail discussion. The criteria tell us that $180^\circ < \theta (H_b(r) - V_b(r)/2 < 0)$ for the SS interactions and $\theta < 180^\circ$ ($H_b(r) - V_b(r)/2 > 0$) for the CS interactions. The CS interactions are subdivided into pure-CS interactions ($p$-CS) of $45^\circ < \theta < 90^\circ$ ($H_b(r) > 0$) and regular-CS interactions ($r$-CS) of $90^\circ < \theta < 180^\circ$ ($H_b(r) < 0$). The $\theta_b$ value predicts the character of interactions. In the pure-CS region of $45^\circ < \theta < 90^\circ$, the character of interactions will be the vDW type for $45^\circ < \theta_b < 90^\circ$ and the typical-HB type with no covalency ($t$-HBm) for $90^\circ < \theta_b < 125^\circ$, where $\theta_b = 125^\circ$ approximately corresponds to $\theta = 90^\circ$. The classical chemical covalent bonds of SS ($180^\circ < \theta$) will be strong when $R > 0.15$ au (Cov-s: strong covalent bonds), whereas they will be weak for $R < 0.15$ au (Cov-w: weak covalent bonds).

The $(R, \theta, \theta_b)$ values are $(0.0576$ au, $184.3^\circ$, $190.9^\circ)$ for the original Br$_2$, if evaluated with MP2/6-311+G(3df). Therefore, the nature of the Br-$\pi$-Br bond in Br$_2$ is classified by the SS interactions ($\theta$ > 180°) and characterized to have the Cov-w nature ($\theta_b > 180^\circ$ and $R < 0.15$ au). The nature is denoted by SS/Cov-w. The $(R, \theta, \theta_b)$ values for the covalent Br-$\pi$-Br bonds in Br$_{2s}$Br$_{12}$ are (0.0472–0.0578 au, 182.0–184.4°, 190.4–192.1°), therefore, the nature is predicted to be SS/Cov-w. The nature of the covalent Br-$\pi$-Br interactions seems not changed so much in the formation of the clusters [44]. The non-covalent Br-$\pi$-Br interactions in Br$_{2s}$Br$_{12}$ are all classified by the pure-CS interactions, since $\theta$ ≤ 76° ($<< 90^\circ$) [44]. The $\theta_b$ values in the C-Lw clusters change systematically. The $\theta_b$ values for $r_2$ in Br$_6$ (C-Lw) ($k = 2$–6) are predicted to be in the range of $91.1^\circ$ ≤ $\theta_b$ ≤ $99.6^\circ$ with $\theta_b = 87.9^\circ$ for Br$_4$ (C-Ls).

However, the values for $r_2$ in Br$_{2s}$ (C-Lw) ($k = 2$–6) are in the range of $90.6^\circ$ ≤ $\theta_b$ ≤ $91.2^\circ$ and the values for the non-covalent interactions other than the edge positions are in the range of $92.1^\circ$ ≤ $\theta_b$ ≤ $93.0^\circ$. Namely, the non-covalent Br-$\pi$-Br interactions are predicted to have the vDW nature (p-CS/vdW) for $r_2$. While, the interactions other than $r_2$ are predicted to have the t-HBm nature (p-CS/t-HBm), since $\theta_b > 90^\circ$. The $\theta_b$ values of $r_2$ for the C-Lw clusters will be less than 90°, irrespective of the angles between $r_1$ and $r_2$, which are close to 180°. The $\theta_b$ values will be larger than 90° for all non-covalent interactions other than $r_2$. Table 1 contains the data for Br$_{10}$ (C$_2$), of which $\theta_b = 90.4^\circ$ ($> 90^\circ$) for $r_2$ and $\theta_b = 87.1^\circ$ ($< 90^\circ$) for $r_4$, although Br$_{10}$ (C$_2$) is not the C-Lw type. The results for $r_2$ seem reasonable based on the structure (cf: Figure 3), while those for $r_4$ would be complex. Table 1 summarizes the predicted nature.

In the case of the non-covalent Br-$\pi$-Br interactions in Br$_3$–Br$_{12}$ other than the C-Lw type clusters, $\theta_b > 90^\circ$ for $r_2$ in Br$_3$ (Si) ($\theta_b = 93.4^\circ$) and Br$_5$ (Si-Wm) ($\theta_b = 94.8^\circ$) and for $r_2$, $r_4$ and $r_5$ in Br$_{12}$ (C$_2$) ($93.4^\circ$ ≤ $\theta_b$ ≤ $93.7^\circ$). The interactions would have the t-HBm nature (p-CS/t-HBm). Very weak non-covalent Br-$\pi$-Br interactions are also detected. The ranges of $64.2^\circ$ ≤ $\theta$ ≤ $66.6^\circ$ and $66.2^\circ$ ≤ $\theta_b$ ≤ $71.2^\circ$ are predicted for $r_2$ and $r_1$ in Br$_{1}$ (C$_{3v}$), $r_2$ in Br$_{1}$ (C$_{2v}$), $r_3$ in Br$_{5}$ (Si-Wm) and $r_7$ and $r_8$ in Br$_{10}$ (C$_{2c}$). The results are summarized in Table 2.

What are the relations between the QTAIM-DFA parameters for the non-covalent Br-$\pi$-Br interactions? The $\theta$ and $\theta_b$ values are plotted versus $R$. The plots are shown in Figure S4 of the Supplementary Materials. They gave very good correlations. The $\theta_b$ values are plotted versus $\theta$. The plot is shown in Figure S5 of the Supplementary Materials. It also gave a very good correlation. Table 3 summarizes the correlations among the QTAIM-DFA parameters.

### Table 3. Correlations in the plots.¹

<table>
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<tr>
<th>Entry</th>
<th>Correlation</th>
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<th>$b$</th>
<th>$R^2$</th>
<th>$n$</th>
</tr>
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<td>1</td>
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<td>0.9999</td>
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</tr>
<tr>
<td>5</td>
<td>$E(2)<em>s$ vs. C$</em>{2v}$</td>
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<td>-182.22</td>
<td>0.997</td>
<td>15⁴</td>
</tr>
<tr>
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<td>$E(2)_s$ vs. $R$</td>
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<td>-29.92</td>
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<tr>
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<td>$E(2)_s$ vs. $\theta_4$</td>
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<td>8</td>
<td>$E(2)_s$ vs. $\theta_5$</td>
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<td>77.17</td>
<td>0.999</td>
<td>15⁴</td>
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</table>

¹ The constants ($a$, $b$, $R^2$) are the correlation constant, the $y$-intercept and the square of correlation coefficient, respectively, in $y=ax+b$. ²Containing TS species. ³Neglecting the data of $r_1$ and $r_3$ in Br$_5$ (C$_{3v}$). ⁴For the non-covalent Br-$\pi$-Br interactions in Br$_5$ (C$_{3v}$)–Br$_{12}$ (C$_{2c}$).
To examine the behavior of the non-covalent Br•-Br interactions, further, NBO analysis is applied to the interactions, next.

3.5. NBO analysis for Br•-Br of Br4 (Cs-L1)–Br12 (Cs-L5)

The non-covalent Br•-Br interactions in Br4 (Cs-L1)–Br12 (Cs-L5) are characterized by σ(3c–4e) of the n(Br)→σ*(Br–Br) type. NBO analysis [46–48] was applied to the n(Br)→σ*(Br–Br) interactions with MP2/6-311+G(3df). For each donor NBO (i) and acceptor NBO (j), the stabilization energy $E(2)$ is calculated based on the second-order perturbation theory in NBO. The $E(2)$ values are calculated according to in Equation (4), where $q_i$ is the donor orbital occupancy, $\epsilon_i$ and $\epsilon_j$ are diagonal elements (orbital energies) and $F(i,j)$ is the off-diagonal NBO Fock matrix element. The values are obtained separately by the contributions from $n_s$(Br)→σ*(Br–Br) and $n_p$(Br)→σ*(Br–Br), which are summarized in Table S5 of the Supplementary Materials. The total values corresponding to $n_s+p$(Br)→σ*(Br–Br) (=$n_s$(Br)→σ*(Br–Br) + $n_p$(Br)→σ*(Br–Br)) are calculated, which are also summarized in Table S5 of the Supplementary Materials. The total values are employed for the discussion.

$$E(2) = q_i \times F(i,j)^2/(\epsilon_j - \epsilon_i) \tag{4}$$

Figure 6 shows the plots of $E(2)$ and $\theta_p$ for the non-covalent Br•-Br interactions in Br4 (Cs-L1)–Br12 (Cs-L5). The values become larger in the order of $P(\mathbf{r}_2$: Br4 (Cs-L1)) < $P(\mathbf{r}_2$: Br6 (Cs-L2)–Br12 (Cs-L5)) < $P(\mathbf{r}_o$: Br8 (Cs-L2)–Br12 (Cs-L5)) < $P(\mathbf{r}_n$: Br8 (Cs-L2)–Br12 (Cs-L5)), where P means $E(2)$ or $\theta_p$, while $\mathbf{r}_o$ and $\mathbf{r}_n$ stand for the last end and the inside non-covalent interactions, respectively, in the sequence (see, Figures 2 and 3). The values for $P = E(2)$ are as follows: $E(2) = 16.6$ kJ mol$^{-1}$ for $\mathbf{r}_2$ in Br4 (Cs-L1) < 17.7 ≤ $E(2) \leq 18.2$ kJ mol$^{-1}$ for $\mathbf{r}_2$ in Br6 (Cs-L2)–Br12 (Cs-L5) < 19.5 ≤ $E(2) \leq 20.0$ kJ mol$^{-1}$ for $\mathbf{r}_o$ in Br6 (Cs-L2)–Br12 (Cs-L5) < 21.2 ≤ $E(2) \leq 22.0$ kJ mol$^{-1}$ for $\mathbf{r}_n$ in Br8 (Cs-L2)–Br12 (Cs-L5).

Figure 6. Plots of $\theta_p$ and $E(2)$ for the non-covalent Br•-Br interactions in Br4 (Cs-L1)–Br12 (Cs-L5). Colours are shown in the figure.

Relations between $E(2)$ and $C_5$ were also examined for the non-covalent Br•-Br interactions in Br4 (Cs-L1)–Br12 (Cs-L5). The $E(2)$ values were plotted versus $C_5^{-1}$ for the non-covalent interactions. Figure 7 shows the plot. The plot gives a very good correlation, which is shown in Table 3 (entry 5).
The results show that the energies for $\sigma(3c-4e)$ of the $n(l)(Br)\rightarrow\sigma^*(Br-Br)$ type in Br$_4$ (C$_v$-L$_1$)–Br$_{12}$ (C$_v$-L$_5$) are well evaluated not only by $E(2)$ but also by $\Delta c$. Similar relations would be essentially observed for the interactions in the non-linear clusters, however, the analyses will be much complex due to the unsuitable structures for the NBO analysis, such as the deviations in the interaction angles expected for Br$_7$, $\sigma(3c-4e)$, the mutual interactions between Br$_7$, and/or the steric effect from other bonds and interactions, placed proximity in space. The $E(2)$ values for Br$_4$ (C$_v$-L$_1$)–Br$_{12}$ (C$_v$-L$_5$) were also plotted versus $R$, $\theta$, and $\delta$, which are shown in Figures S6–S8, respectively, of the Supplementary Materials. The plots gave very good correlations, which are given in Table 3 (entries 6–8).

Figure 7. Plot of $E(2)$ versus $1/C_0$ for the non-covalent Br--*Br interactions in Br$_4$ (C$_v$-L$_1$)–Br$_{12}$ (C$_v$-L$_5$).

3.6. MO descriptions for non-covalent Br--*Br interactions in Br$_4$

As discussed above, Br$_4$ $\sigma(3c-4e)$ of the $n(l)(Br)\rightarrow\sigma^*(Br-Br)$ type plays an important role in the formation of Br$_4$ (C$_v$-L$_1$)–Br$_{12}$ (C$_v$-L$_5$). However, there must exist some interactions, other than Br$_4$ $\sigma(3c-4e)$, to stabilize the clusters. The $\Delta E_{BS}$ values for Br$_4$ (C$_v$, $n(l)(Br)$ and Br$_4$ (D$_{2h}$) (–9.1 kJ mol$^{-1}$) are not so different from that for Br$_4$ (C$_v$-L$_1$) (–10.7 kJ mol$^{-1}$). However, Br$_4$ (C$_v$) and Br$_4$ (D$_{2h}$) must consist of the interactions, other than $\sigma(3c-4e)$. Indeed, Br$_4$ $\sigma(3c-4e)$ of the $n(\text{Br})\rightarrow\sigma^*(\text{Br--Br})$ type contributes to stabilise Br$_4$ (C$_v$-L$_1$), but Br$_4$ (C$_v$) and Br$_4$ (D$_{2h}$) are shown to be stabilised by the $\sigma(\text{Br--Br})\rightarrow\sigma^*\text{Ry(Br)}$ interaction by NBO, where Ry stands for the Rydberg term, although not shown.

The total energy for a species ($E$) is given by the sum of the core terms ($H(i)$) over all electrons, $\Sigma_{i} H(i)$ and the electron-electron repulsive terms, $(\Sigma_{i<j} |\phi_i\rangle - \Sigma_{i<j} |\phi_j\rangle |\phi_j\rangle)/2$, as shown by Equation (5), where $H(i)$ consists of the kinetic energy and electron-nuclear attractive terms for electron $i$. $E$ contains the nuclear-nuclear repulsive terms, although not clearly shown in Equation (5). As shown in Equation (6), the sum of MO energy for electron $i$, $\epsilon_i$, over all electrons, $\Sigma_{i} \epsilon_i$, will be larger than $E$ by $(\Sigma_{i<j} |\phi_i\rangle - \Sigma_{i<j} |\phi_j\rangle |\phi_j\rangle)/2$, since the electron-electron repulsions are doubly counted in Equation (6). Therefore, $\Sigma_{i} H(i)$ and $(\Sigma_{i<j} |\phi_i\rangle - \Sigma_{i<j} |\phi_j\rangle |\phi_j\rangle)/2$ are given separately by Equations (7) and (8), respectively. The $\epsilon$ values for Br$_4$ (C$_v$), Br$_4$ (D$_{2h}$) and 2Br$_2$, together with Br$_4$ (C$_v$-L$_1$), are collected in Tables S6–S9, respectively, of the Supplementary Materials, for convenience of discussion. Parameters ($\Delta^\sigma$) in the formation of Br$_4$ from the components are evaluated according to Equation (9). The $\Delta^\sigma$ $H(i)$ and $\Delta(\Sigma_{i<j} |\phi_i\rangle - \Sigma_{i<j} |\phi_j\rangle |\phi_j\rangle)/2$ values for the formation of Br$_4$ (C$_v$), Br$_4$ (D$_{2h}$) and Br$_4$ (C$_v$-L$_1$) are collected in Table S11 of the Supplementary Materials.
The energy profiles of Br$\text{Br}$ are shown in Figure 8. Contributions from $\Delta \Sigma^a H(i) (\Delta P = B)$ and $\Delta (\Sigma^a n^a_j - \Sigma^a n^a K_0)/2 (\Delta P = C)$ to $\Delta ES (\Delta P = D)$, magnified by 10 times in the plot) for Br$_4$ (C-s-Li), Br$_4$ (C-s) and Br$_4$ (D-s), relative to 2Br$_2$, together with $\Delta \Sigma^a \varepsilon$ ($\Delta P = A$).

The energy profiles of Br$_4$ (C-s) and Br$_4$ (D-s) seem very different from that of Br$_4$ (C-s-Li). The $\Delta \Sigma^a \varepsilon$ terms for Br$_4$ (C-s) and Br$_4$ (D-s) are evaluated to be 587.5 and 908.1 kJ mol$^{-1}$, respectively.
Therefore, no MOs essentially stabilize Br. Figure 10 illustrates the interactions to produce HOMO, HOMO-3, HOMO-4 and HOMO-7. Consequently, it is difficult to explain the stability of Br (C₉₆) and Br (D₂₉), based on the MO energies. On the other hand, $\Delta \Sigma_\pi^e H_{\pi}(i)$ of Br (C₉₆) and Br (D₂₉) are evaluated to be -603.5 and -926.3 kJ mol⁻¹, respectively, whereas $\Delta \Sigma_{\delta}^e J_{ij} - \sum_{\delta}^e K_0^2/2$ are 595.5 and 917.2 kJ mol⁻¹, respectively. As a result, the ($\Delta \Sigma_\pi^e H_{\pi}(i) + \Delta \Sigma_\delta^e J_{ij} - \sum_{\delta}^e K_0^2/2$) values are -8.0 and -9.1 kJ mol⁻¹ for Br (C₉₆) and Br (D₂₉), respectively, which correspond to their $\Delta E_{\pi}$ values, respectively (relative to 2E(Br)). The results show that the stabilizing effect by $\Delta \Sigma^e H_{\pi}(i)$ overcomes the shorter electron-nuclear distances in the species in the average. The shorter electron-electron distances must destabilize Br (C₉₆) and Br (D₂₉) through the factor of $\Delta \Sigma_{\delta}^e J_{ij} - \sum_{\delta}^e K_0^2/2$, which is the inverse effect form the electron-nuclear interaction on $\Delta \Sigma^e H_{\pi}(i)$. However, the effect of the shorter distances on $\Delta \Sigma_{\delta}^e J_{ij} - \sum_{\delta}^e K_0^2/2$ in Br (C₉₆) and Br (D₂₉), although not so large.

How can the BPs in Br (C₉₆) and Br (D₂₉) be rationalized through the orbital interactions? The $\Delta \xi$ values of Br (C₉₆) are positive for all occupied MOs, relative to the corresponding values of 2Br, except for HOMO-3 (-5.5 kJ mol⁻¹), HOMO-6 (-2.9 kJ mol⁻¹), HOMO-7 (-35.8 kJ mol⁻¹) and HOMO-13 (-1.1 kJ mol⁻¹). Figure 9 illustrates the interactions to produce HOMO, HOMO-3, HOMO-4 and HOMO-7. Indeed, HOMO-7 seems well contribute to stabilize Br (C₉₆), but HOMO-4 (+40.8 kJ mol⁻¹) is also formed in the $\pi(Br) - \pi(Br)$ mode. Similarly, HOMO (+13.7 kJ mol⁻¹) is formed, together with HOMO-3 in the $\pi^*(Br) + \pi^*(Br)$ mode. Therefore, all MOs seem not to contribute to stabilize Br (C₉₆), inherently. Nevertheless, HOMO, HOMO-4 and HOMO-7 seem to rationalize the appearance of BPs in Br (C₉₆), along the diagonal line and shorter sides of the parallelogram, although all electrons contribute to appear BPs in molecules.

Similarly, $\Delta \xi$ of Br (D₂₉) are positive for all occupied MOs, relative to the corresponding values of 2Br, except for HOMO-3 (-1.9 kJ mol⁻¹), HOMO-7 (-39.2 kJ mol⁻¹) and HOMO-13 (-0.5 kJ mol⁻¹). Figure 10 illustrates the interactions to produce HOMO, HOMO-3, HOMO-4 and HOMO-7 in Br (D₂₉). HOMO-4 (+50.2 kJ mol⁻¹) is formed through the $\pi(Br) - \pi(Br)$ mode, in addition to HOMO-7. Similarly, HOMO (+13.9 kJ mol⁻¹) is formed, accompanied by HOMO-3 in the $\pi^*(Br) + \pi^*(Br)$ mode. Therefore, no MOs essentially stabilize Br (D₂₉). However, the appearance of BPs along the longer

![Figure 9. Energy profile for the formation of Br6 (C₉₆), exemplified by HOMO, HOMO-3, HOMO-4 and HOMO-7.](image)

![Figure 10. Energy profile for the formation of Br6 (D₂₉), exemplified by HOMO, HOMO-3, HOMO-4 and HOMO-7.](image)
and shorter diagonal lines of the tetrahedron of Br$_4$ ($D_2d$) seem to be rationalized by HOMO-7, together with HOMO-3 and HOMO-4, modifying the BPs, although BPs will appear as the whole properties of molecules.

The nature of interactions in the charged clusters must also be of very interest. Such investigations are in progress.

4. Conclusions

The intrinsic dynamic and static nature of the non-covalent Br-Br interactions was elucidated for Br$_n$-Br$_0$ with MP2/6-311+G(3df). QTAIM-DFA was applied to the investigation. $H_0(r)$ is plotted versus $H_0(r) - V_{el}(r)/2$ for the interactions at BCPs of the fully optimized structures, together with those from the perturbed structures, generated with CIV. The nature of the covalent Br-Br bonds in Br$_n$-Br$_0$ is predicted to have the SS/Cov-w nature if calculated with MP2/6-311+G(3df). On the other hand, the nature of the non-covalent Br-Br interactions in Br$_n$-Br$_2$ is classified by the pure-CS interactions ($\theta \leq 76^\circ$). The non-covalent Br-Br interactions in the linear type clusters of Br$_4$ (C$_{L1}$)-Br$_2$ (C$_{L2}$); are predicted to have the p-CS/t-HBVs nature ($90.6^\circ \leq \theta$), except for $r_2$ outside ones of the first, which have the p-CS/vdW nature, although it is very close to the border area between the two ($68.9^\circ \leq \theta$). In the case of the cyclic clusters, the non-covalent Br-Br interactions will have the p-CS/vdW nature ($\theta \leq 88.4^\circ$), except for $r_2$ in Br$_8$ ($S_4$) ($\theta_1 = 93.5^\circ$) and Br$_8$ ($S_4$-Wm) ($\theta_4 = 95.3^\circ$), which have the p-CS/t-HBVs nature.

The energy for Br$_5$ $\sigma$(3c-4e) of the $n_4$(Br) $\rightarrow \sigma^*$(Br-Br) type are well evaluated by not only $E(2)$ but also $C_{r^{-1}}$ for Br$_5$ (C$_{L1}$)-Br$_2$ (C$_{L3}$). $E(2)$ correlates very well to $C_{r^{-1}}$. The CT interactions of the $n_4$(Br) $\rightarrow \sigma^*$(Br-Br) type must contribute to form Br$_5$ (C$_{L1}$), which can be explained based on the MO energies, $\omega$. However, it seems difficult to explain the stability of Br$_4$ (C$_{2v}$) and Br$_8$ (D$_{2h}$) based on the energies. The Br$_2$ molecules must be stacked more effectively in Br$_4$ (C$_{2v}$) and Br$_8$ (D$_{2h}$), resulting in the shorter electro-nuclear distances in the average. The energy lowering effect by $\Delta \omega$ $H_s(i)$, due to the effective stacking of 2Br in Br$_4$ (C$_{2v}$) and Br$_8$ (D$_{2h}$), must contribute to form the clusters, although the inverse contribution from $\Delta((\Sigma n^i_j - \Sigma n^i_j K_{ij})/2$ must also be considered.

Supplementary Materials: The following are available online at www.mdpi.com/xxx, Table S1: Structural parameters for Br$_n$-Br$_0$, Table S2: Structural parameters for Br$_n$-Br$_2$, Table S3: The bond path distances and the straight-line distances in the polybromine clusters, together with the differences between the two, Table S4: QTAIM functions and QTAIM-DFA parameters for Br-Br in polybromine clusters of Br$_n$-Br$_2$, Table S5: Contributions from the donor-acceptor (NBO(i) $\rightarrow$ NBO(j)) interactions of the $n$(Br) $\rightarrow \sigma^*$(Br-Br) type in the optimized structures of Br$_n$-Br$_2$ calculated with the NBO analysis, Table S6: MO energies of Br$_4$ (C$_{2v}$), Table S7: MO energies of Br$_5$ (C$_{2v}$), Table S8: MO energies of Br$_6$ (D$_{2h}$), Table S9: MO energies of Br$_8$ (C$_{2v}$), Table S10: The $\Delta\omega$ values for Br$_4$ (C$_{2v}$), relative to 2Br$_2$ (D$_{2h}$), Table S11: Energies for the Br$_4$ clusters and 2Br$_2$, together with the differences between the two, Figure S1: Plot of $\Delta E_{\omega}$ versus $\Delta E_{\omega}$ for Br$_4$-Br$_2$, relative to those of Br$_2$, respectively, Figure S2: Plots of $\Delta E_{\omega}$ for Br$_5$-Br$_2$ (C$_{2v}$), Figure S3: Optimized structures for the cyclic bromine clusters of Br$_n$-Br$_2$, together with the linear type bromine cluster of Br$_0$, Figure S4: Plot of $\Delta E_{\omega}$ versus $R$ for the non-covalent Br-Br interactions at the BCPs in the fully optimized structures of Br$_n$-Br$_2$, Figure S5: Plot of $\theta_4$ versus $\theta_4$ for the non-covalent Br-Br interactions at the BCPs in the fully optimized structures of Br$_n$-Br$_2$, Figure S6: Plot of $E(2)$ versus $R$ for the non-covalent Br-Br interactions in Br$_8$ (C$_{2v}$)-Br$_2$ (C$_{2v}$), Figure S7: Plot of $E(2)$ versus $\theta_4$ for the non-covalent Br-Br interactions in Br$_8$ (C$_{2v}$)-Br$_2$ (C$_{2v}$), Figure S8: Plot of $E(2)$ versus $\theta_4$ for the non-covalent Br-Br interactions in Br$_8$ (C$_{2v}$)-Br$_2$ (C$_{2v}$), Figure S9: MO: ($i = 70, 67, 64, 35$ and $30$) and the energies relative to those corresponding to 2Br$_2$, and Cartesian coordinates and energies of all the species involved in the present work. Appendix: Survey of QTAIM, closely related to QTAIM dual functional analysis, Criteria for classification of interactions: behavior of typical interactions elucidated by QTAIM-DFA, Characterization of interactions.

Acknowledgments: This work was partially supported by a Grant-in-Aid for Scientific Research (No. 26410050) from the Ministry of Education, Culture, Sports, Science and Technology of Japan. Theoretical calculations were partially performed using Research Center for Computational Science, Okazaki, Japan.
Author Contributions: S.H. and W.N. formulated the project. S.H., W.N. and T.N. optimized all compounds. T.N. and E.T. calculated the QTAIM functions and evaluated the QTAIM-DFA parameters and analyzed the data. S.H. and W.N. wrote the paper, while T.N. and E.T. organized the data to assist the writing.

Conflicts of Interest: The authors declare no conflict of interest.

References
15. The workshop entitled “Categorizing Halogen Bonding and other Noncovalent Interactions Involving Halogen Atoms” was organized as a satellite event of the XXII Congress and General Assembly of the International Union of Crystallography.


29. The basic concept for the compliance constants was introduced by Taylor and Pitzer [49], followed by Konkoli and Cremer [50].

30. The $C_i$ are defined as the partial second derivatives of the potential energy due to an external force, as shown in Equations (R1) [31–33], where $i$ and $j$ refer to internal coordinates, and the external force components acting on the system $f_i$ and $f_j$ correspond to $i$ and $j$, respectively.

$$C_{ij} = \frac{\partial^2 E}{\partial f_i \partial f_j}$$  \hspace{1cm} (R1)

The $C_{ij}$ values and the coordinates corresponding to $C_{ij}$ were calculated by using the Compliance 3.0.2 program released by Grunenberg, J. and Brandhorst, K. http://www.oc.tubs.de/Grunenberg/compliance.html.


42. The AIM2000 program (Version 2.0) is employed to analyze and visualize atoms-in-molecules: Biegler-König, F. Calculation of atomic integration data. *J. Comput. Chem.* **2000**, *21*, 1040–1048; see also refs [26] and [27].
44. The Br–Br distance in Br₂ was optimized to be 2.2806 Å with MP2/6-311+G(3df), which was very close to the observed distance in the gas phase (2.287 Å). However, the values are shorter than that determined by the X-ray crystallographic analysis (2.491 Å) by 0.210 Å. The non-covalent Br–Br distance is 3.251 Å in crystal, which is shorter than the sum of the van der Waals radii [51] by 0.45 Å.
45. The molecular graph for Br₄ (C₄h) was very complex and very different from that expected for it when calculated with MP2/6-311+G(3df)/MP2/6-311+G(3df). Some (ω, σ) = (3, −3) attractors appear in the molecular graph of Br₄ (C₄h), which do not correspond to bromine atoms. Therefore, the molecular graph for Br₄ (C₄h) were drawn with MP2/6-311+G(d)/MP2/6-311+G(3df), which was shown in Fig. 2. The QTAIM functions were calculated with the same method.