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 *

Faculty of Systems Engineering, Wakayama University, 930 Sakaedani, Wakayama 640-8510, Japan; s209004@wakayama-u.ac.jp (T.N.); s216156@wakayama-u.ac.jp (E.T.)
* Correspondence: hayashi3@sys.wakayama-u.ac.jp (S.H.); nakanisi@sys.wakayama-u.ac.jp (W.N.); Tel.: +81-73-457-8252 (S.H. & W.N.)

Abstract: The intrinsic dynamic and static nature of noncovalent Br←Br interactions in neutral polybromine clusters is elucidated for Br$_2$–Br$_{12}$, 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 the interactions. The intrinsic dynamic nature originates from those of the perturbed structures generated using the coordinates derived from the compliance constants for the interactions and the fully optimized structures. The noncovalent 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 σ(Br)→σ*(Br–Br) interactions. The compliance constants for the corresponding noncovalent interactions are strongly correlated to the E(2) values based on NBO. Indeed, the MO energies seem not to contribute to stabilizing Br$_4$ (C$_3$h) and Br$_4$ (D$_{2d}$), but the core potentials stabilize them, relative to the case of 2Br$_2$; this is possibly due to the reduced nuclear-electron distances, on average, for the dimers.

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 relevant to halogen bonding has been accumulated so far [3]. Halogen bonding has been 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: symmetric (type I) and bent (type II) geometries. The bonding has also been investigated in the liquid [7,8] and gas [9] phases. The nature of halogen bonding has been discussed based on the theoretical background on the molecular orbital description for the bonding and the σ-hole developed on the halogen atoms, together with the stability of the structural aspects [10]. We also reported the dynamic and static nature of Y–X←π(C$_6$H$_6$) interactions recently [11]. Halogen bonding is applied to a wide variety of fields in chemical and biological sciences, such as crystal engineering, supramolecular soft matters, and nanoparticles. Efforts have been made to unify and categorize the accumulated results and establish the concept of halogen bonding [3,12–15].

Structures of halogen molecules (X$_2$) have been reported, as determined by X-ray crystallographic analysis for X = Cl, Br, and I [16–18]. The behavior of bromine–bromine interactions has been reported for the optimized structures of Br$_2$–Br$_5$ in the neutral and/or charged forms, together with Br$_1$, so far [19,20]. Figure 1 draws the observed structure of Br$_2$, for example. The bromine molecules seem to exist as a zig-zag structure in the infinite chains in crystals. One would find the linear alignment of three Br atoms in an
L-shaped dimer ((Br$_2$)$_2$; Br$_4$) and the linear alignment of four Br atoms in a double L-shaped trimer ((Br$_2$)$_3$; Br$_6$) 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 construct linear infinite chains. The attractive np(Br)→σ*(Br–Br) σ(3c–4e) (three center–four electron interaction of the σ-type) and np$_p$(Br)→σ*(Br–Br)←np$_p$(Br) σ(4c–6e) must play a very important role to stabilize Br$_4$ and Br$_6$, respectively, where np$_p$(Br) stands for the p-type nonbonding orbital of Br in the plane, perpendicular to the molecular Br$_2$ axis, and σ*(Br–Br) is the σ*-orbital of Br$_2$. The crystal structures of Cl$_2$ and I$_2$ are very similar to that of Br$_2$.

Figure 1. Structure of Br$_2$, determined by X-ray crystallographic analysis [17].

We have been very interested in the behavior of halogen bonding in polyhalogen clusters, together with the structures. How can the interactions in the polyhalogen clusters be clarified? We propose QTAIM dual-functional analysis (QTAIM-DFA) [21–25] based on the quantum theory of atoms in molecules (QTAIM) approach introduced by Bader [26,27] to classify and characterize the various interactions effectively [28]. In QTAIM-DFA, $H_0(r_c)$ are plotted versus $H_0(r_c) - V_b(r_c)/2 = (l^2/8m)\nabla^2 \rho_b(r_c)$ (see Equation (SA2) in the supplementary materials), where $\rho_b(r_c)$, $H_0(r_c)$, and $V_b(r_c)$ stand for the charge densities, total electron energy densities, and potential energy densities, respectively, at bond critical points (BCPs, *) on the bond paths (BPs) in this paper [26]. The kinetic energy densities at BCPs will be similarly denoted by $G_b(r_c)$ [26]. A chemical bond or an interaction between Br and Br is denoted by Br-Br in this work, where the asterisk emphasizes the existence of a BCP on a BP for Br–Br [26,27]. 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 polar coordinate ($\theta$, $\rho$) 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 ($\theta_p$, $\kappa_p$), where $\theta_p$ corresponds to the tangent line and $\kappa_p$ is the curvature of the plot. $\theta$ and $\theta_p$ are measured from the $y$-axis and the $y$-direction, respectively. We call ($\theta$, $\rho$) and ($\theta_p$, $\kappa_p$) the QTAIM-DFA parameters [29].

Interactions are classified by the signs of $\nabla^2 \rho_b(r_c)$ and $H_0(r_c)$, based on the QTAIM approach. The interactions are called shard shell (SS) interactions when $\nabla^2 \rho_b(r_c) < 0$ and closed-shell (CS) interactions when $\nabla^2 \rho_b(r_c) > 0$ [26]. In particular, CS interactions are called pure CS (p-CS) interactions when $H_0(r_c) > 0$ and $\nabla^2 \rho_b(r_c) > 0$. We call interactions where $H_0(r_c) < 0$ and $\nabla^2 \rho_b(r_c) > 0$ regular CS (r-CS) interactions, which clearly distinguishes
these interactions from the $p$-CS interactions. The signs of $\nabla^2 \rho_b(r_c)$ can be replaced by those of $H_b(r_c) - V_b(r_c)/2$ because $(\hbar^2/8m)\nabla^2 \rho_b(r_c) = H_b(r_c) - V_b(r_c)/2$ (see Equation (SA2) in the auxiliary information). Indeed, $H_b(r_c) - V_b(r_c)/2 = 0$ corresponds to the borderline between the classic covalent bonds of SS and the noncovalent interactions of CS, but $H_b(r_c) = 0$ appears to be buried in the noncovalent interactions of CS. As a result, it is difficult to characterize the various CS interactions based on the signs of $H_b(r_c) - V_b(r_c)/2$ and/or $H_b(r_c)$. In QTAIM-DFA, the signs of the first derivatives of $H_b(r_c) - V_b(r_c)/2$ and $H_b(r_c)$ $(d(H_b(r_c) - V_b(r_c)/2)/dr) \text{ and } dH_b(r_c)/dr$, respectively, where $r$ is the interaction distance) are used to characterize CS interactions, in addition to those of $H_b(r_c) - V_b(r_c)/2$ and $H_b(r_c)$, after analysis of the plot. While the former corresponds to $(\theta_p, \kappa_p)$, the latter does to $(R, \theta)$. The analysis of the plots enables us to characterize the various CS interactions more effectively. Again, the details are explained later.

The perturbed structures necessary for QTAIM-DFA can be generated. Among them, a method employing the coordinates corresponding to the compliance constants $C_{ij}$ for internal vibrations is shown to be highly reliable to generate the perturbed structures [30–39]. The method, which we proposed recently, is called CIV. 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 halogen–halogen interactions in the polyhalogen clusters. As the first step to clarify the nature of various types of 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 structures and 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

The structures were optimized by employing Gaussian 09 programs [40]. The 6-311+G(3df) basis [41–44] set was applied to optimize the structures of neutral polybromine clusters, Br$_2$–Br$_3$. The Møller–Plesset second-order energy correlation (MP2) level [45–47] was applied for the optimizations. Optimized structures were confirmed by frequency analysis. The results of the frequency analyses were employed to calculate the $C_{ij}$ values and coordinates corresponding to $C_{ij}$ [30,34–36]. The $\rho_b(r_c)$, $H_b(r_c) - V_b(r_c)/2$ (=$(\hbar^2/8m)\nabla^2 \rho_b(r_c)$), and $H_b(r_c)$ values were calculated using the Gaussian 09 program package [40], with the same method applied to the optimizations. Data were analyzed with the AIM2000 [48,49] and AIMAll [50] programs.

Coordinates corresponding to the compliance constants for an internal coordinate $i$ of the internal vibrations ($C_i$) 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. An $i$-th perturbed structure in question ($S_{iw}$) was generated by the addition of the coordinates ($C_i$) corresponding to $C_{ij}$ to the standard orientation of a fully optimized structure ($S_o$) in the matrix representation. The coefficient $g_{iw}$ in Equation (1) controls the difference in structures between $S_{iw}$ and $S_o$: $g_{iw}$ are determined to satisfy Equation (2) for the interaction in question, where $r$ and $r_o$ show the distances in question in the perturbed and fully optimized structures, respectively, with $\alpha_o$ of Bohr radius (0.52918 Å) [21–25,30].

$$S_{iw} = S_o + g_{iw} \times C_i$$  \hspace{1cm} (1)
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were optimized for Br with MP2/6-311+G(3df) [51]. The energies for the formation of BrC (∆E(s)) and between Br and Br12 are optimized for BrC (∆E(s)) and between Br and Br12 are optimized in Tables S1 and S2, respectively. Some transition states (TSs) for BrC and Br12 were also calculated. The notation of C-Lm (m = 1–5) is used for the linear L-shaped clusters of the Cn symmetry, where m stands for the number of noncovalent interactions in Br2m+2 (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 ρ(r) for the linear-type bromine clusters Br4–Br12 (C4v-Lm (m = 1–5)) and for the cyclic bromine clusters Br4–Br12, drawn on the optimized structures with MP2/6-311+G(3df) [51]. The energies for the formation of Br4–Br6 and Br8–Br12 are given in Tables S1 and S2, respectively, from the components (ΔE = E(Br2)+kE(Br2)) on the energy surfaces (ΔEES) and those with the collections of zero-point energies (ΔEZP). The ΔEZP values were plotted versus ΔEES. The plot is shown in Figure S1, which gives an excellent correlation (y = 0.940x + 0.129; R2 (square of correlation coefficient) = 0.99999) [52]. Therefore, the ΔEES values are employed for the discussion.

The behavior of the neutral dibromine clusters (Br4) is discussed first. Three structures were optimized for Br4 as minima with some TSs. The minima are the L-shaped structure of C4v symmetry (Br4 (C4v-L1)) [19], the cyclic structure of C2h symmetry (Br4 (C2h)), and the tetrahedral type of D2d symmetry (Br4 (D2d)). A TS of the C4v symmetry was detected between Br4 (C4v-L1) and Br4 (C2h), and two TSs of the C1 symmetry were between Br4 (C2h) and Br4 (D2d) and between Br4 (D2d) and Br4 (C2-L1). They are called TS (C4v: C2h, C2d), TS (C1: C2h, D2d), and TS (C1: D2d, C2h), respectively. The three minima will be converted to each other through the three TSs. A TS between Br4 (C4v-L1) and its topological isomer was also detected, which is called TS (C4v: C2h, C2d); however, further effort was not made to search for similar TSs between Br4 (C2h) and its topological isomer and between Br4 (C2d) and its topological isomer.

Figure 2 draws the energy profiles for the optimized structures of minima, Br4 (C4v-L1), Br4 (C2h), and Br4 (D2d), together with the TSs TS (C4v: C2h, C2d), TS (C4v: C2h, D2d), TS (C1: C2d, C2h), and TS (C2v: C2h, C2d). The optimized structures are not shown in the 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 ΔEES value of −10.7 kJ mol−1 for the formation of Br4 (C4v-L1) seems very close to the border area between the vdW and typical hydrogen bond (t-HB) adducts. The driving force for the formation of Br4 (C4v-L1) must be Br3 σ(3c–4e) of the nπ(Br)→π*(Br–Br) type. The interactions in Br4 (C2h) and Br4 (D2d) seem very different from those in Br4 (C4v-L1). The ΔEES values of Br4 (C2h) (−8.0 kJ mol−1) and Br4 (D2d) (−9.1 kJ mol−1) are close to that for Br4 (C4v-L1) (−10.7 kJ mol−1). Moreover, the values for TS (C4v: C2h, C2d) (−7.4 kJ mol−1), TS (C1: C2h, D2d) (−7.6 kJ mol−1), TS (C1: D2d, C2h) (−7.0 kJ mol−1), and TS (C2v: C2h, C2d) (−8.7 kJ mol−1) are not so different from those for the minima.

3. Results and Discussion

3.1. Structural Optimizations of Polybromine Clusters, Br6–Br12

Structures of the neutral Br2–Br12 clusters were optimized with MP2/6-311+G(3df). The structural parameters for the optimized structures of minima for Br2–Br6 and Br8–Br12 are collected in Tables S1 and S2, respectively. Some transition states (TSs) for Br6 were also calculated. The notation of C-Lm (m = 1–5) is used for the linear L-shaped clusters of the Cn symmetry, where m stands for the number of noncovalent interactions in Br2m+2 (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 ρ(r) for the linear-type bromine clusters Br4–Br12 (C4v-Lm (m = 1–5)) and for the cyclic bromine clusters Br4–Br12, drawn on the optimized structures with MP2/6-311+G(3df) [51]. The energies for the formation of Br4–Br6 and Br8–Br12 are given in Tables S1 and S2, respectively, from the components (ΔE = E(Br2)+kE(Br2)) on the energy surfaces (ΔEES) and those with the collections of zero-point energies (ΔEZP). The ΔEZP values were plotted versus ΔEES. The plot is shown in Figure S1, which gives an excellent correlation (y = 0.940x + 0.129; R2 (square of correlation coefficient) = 0.99999) [52]. Therefore, the ΔEES values are employed for the discussion.

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Figure 2 draws the energy profiles for the optimized structures of minima, Br4 (C4v-L1), Br4 (C2h), and Br4 (D2d), together with the TSs TS (C4v: C2h, C2d), TS (C4v: C2h, D2d), TS (C1: C2d, C2h), and TS (C2v: C2h, C2d). The optimized structures are not shown in the 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 ΔEES value of −10.7 kJ mol−1 for the formation of Br4 (C4v-L1) seems very close to the border area between the vdW and typical hydrogen bond (t-HB) adducts. The driving force for the formation of Br4 (C4v-L1) must be Br3 σ(3c–4e) of the nπ(Br)→π*(Br–Br) type. The interactions in Br4 (C2h) and Br4 (D2d) seem very different from those in Br4 (C4v-L1). The ΔEES values of Br4 (C2h) (−8.0 kJ mol−1) and Br4 (D2d) (−9.1 kJ mol−1) are close to that for Br4 (C4v-L1) (−10.7 kJ mol−1). Moreover, the values for TS (C4v: C2h, C2d) (−7.4 kJ mol−1), TS (C1: C2h, D2d) (−7.6 kJ mol−1), TS (C1: D2d, C2h) (−7.0 kJ mol−1), and TS (C2v: C2h, C2d) (−8.7 kJ mol−1) are not so different from those for the minima.
In the case of Br₆, three structures of the linear C₈ symmetry (Br₆ (C₈-L₂)), the linear C₂ symmetry (Br₆ (C₂)), and the cyclic C₃h symmetry (Br₆ (C₃h-c)) were optimized typically as minima. The linear Br₆ clusters of C₂h symmetry (Br₆ (C₂h)) and Cᵥ symmetry (Br₆ (Cᵥ)), similar to Br₅ (Cᵥ), were also optimized, of which the torsional angles, φ₁(Br²Br³Br⁴Br) (=φ₃), were 0° and 180°, respectively. One imaginary frequency was detected for each; therefore, they are assigned to TSs between Br₅ (Cᵥ) and the topological isomer on the different reaction coordinates. Further effort was not made to search for TSs.

The ∆E_ES value for Br₅ (C₈-L₂) was predicted to be −22.6 kJ mol⁻¹. The magnitude is slightly larger than the double value for Br₄ (C₈-L₁) (∆E_ES = −10.7 kJ mol⁻¹). Two types of σ (3c–4e) operate to stabilize Br₆ (C₈-L₂). One, σ(3c–4e), seems similar to that in Br₄ (C₈-L₁), but the other would be somewhat different. Namely, the second interaction would contribute to ∆E_ES somewhat more than that of the first one in the formation of Br₆ (C₈-L₂). On the other hand, the linear interaction in Br₆ (C₂) can be explained by σ(4c–6e) of the nₚ(Br) → σ*(Br–Br)← nₚ(Br) type. The magnitude of ∆E_ES of Br₅ (C₂) seems slightly smaller than that of Br₆ (C₈-L₂) but is very close to the double value for Br₄ (C₈-L₁). The magnitude of ∆E_ES for Br₆ (C₃h-c) is close to the triple value of Br₄ (C₈-L₁). One finds triply degenerated σ(3c–4e) interactions in Br₆ (C₃h-c). The similarity in the interactions for Br₅ (C₈-L₁), Br₅ (C₂), and Br₆ (C₃h-c) will be discussed again later. The magnitudes of ∆E_ES become proportionally larger to the size of the clusters, as shown in Figures S1 and S2. The ∆E_ES values are plotted versus k in Br₂k (2 ≤ k ≤ 6) for the C₈-Lₘ type. The results are shown in Figure S2. Contributions from inner σ(3c–4e) (named rₐ(n)) to ∆E_ES seem slightly larger than those from σ(3c–4e) in the front end and end positions (named r₂ and rₐ, respectively).

After examination of the optimized structures, the next extension is to clarify the nature of 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 contour maps of ρ(r) for the linear type of Br₄ (C₈-L₁)–Br₁₂ (C₈-L₅), drawn on the structures optimized with MP2/6-311+G(3df). Figure 4 draws the molecular graphs with contour maps of ρ(r) for Br₃–Br₁₂, other than those for Br₄ (C₈-L₁)–Br₁₂ (C₈-L₅), calculated with MP2/6-311+G(3df) [53,54] (see also Figure S3). All BCPs expected are detected clearly, together with RCPs and a CCP containing those for noncovalent Br⁺Br interactions, which are located at the (three-dimensional) saddle points of ρ(r).
Figure 3. Molecular graphs with contour plots of $\rho(r)$ for the linear-type bromine clusters of Br$_4$–Br$_{12}$, calculated with MP2/6-311+G(3df). (a–e) for the linear Cs-Lm type, (f, g) for the C$_2$ type, and (h) for the notations of atoms, bonds, and angles, exemplified by B$_{12}$ (Cs-L$_5$). 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) by pink lines. See ref. [51] for (a).

3.3. Survey of the Br-*Br Interactions in Polybromine Clusters

As shown in Figures 2–4, the 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, together with the differences...
between them, \( \Delta r_{\text{BP}} = r_{\text{BP}} - R_{\text{SL}} \). The magnitudes of \( \Delta r_{\text{BP}} \) are less than 0.01 Å, except for \( r_2 \) in Br₄ (C₂ᵥ) (\( \Delta r_{\text{BP}} = 0.014 \) Å), \( r_3 \) in Br₈ (S₄-Wm) (0.014 Å), and \( r_2 \) in Br₁₀ (C₂₋c) (0.012 Å). Consequently, all BPs in Br₂–Br₁₂ can be approximated as straight lines.

The \( \rho_b(r_c) \), \( H_b(r_c) - V_b(r_c)/2 = (\hbar^2/8m)\nabla^2\rho_b(r_c) \), and \( H_b(r_c) \) values are calculated for the Br⁺–Br interactions at BCPs in the structures of Br₂–Br₁₂, optimized with MP2/6-311+G(3df). Table 1 collects the values for the noncovalent Br⁺–Br interactions in Br₄–Br₁₂ of the C₄ᵥ–L₄ type. Table 2 summarizes the values for the noncovalent Br⁺–Br interactions in Br₄–Br₁₂, other than those of the C₄ᵥ–L₄ type. \( H_b(r_c) \) are plotted versus \( H_b(r_c) - V_b(r_c)/2 \) 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 noncovalent Br⁺–Br interactions and covalent Br⁺–Br bonds, exemplified by Br₁₀ (C₂₋L₄).

### Table 1. The \( \rho_b(r_c) \), \( H_b(r_c) - V_b(r_c)/2 = (\hbar^2/8m)\nabla^2\rho_b(r_c) \), and \( H_b(r_c) \) values and QTAIM-DFA parameters for Br⁺–Br at BCPs in Br₄ (C₂₋L₄)–Br₁₂ (C₄ᵥ–L₄), together with Br₁₀ (C₂) and Br₂, evaluated with MP2/6-311+G(3df).

| Species (Symmetry) | BCP on | \( \rho_b(r_c) \) (au) | \( c\nabla^2\rho_b(r_c) \) (au) | \( H_b(r_c) \) (au) | \( R \) (Å) | \( \theta \) (°) |
|--------------------|--------|------------------------|------------------------|-----------------|---------|---------|
| Br₂ (C₂₋L₄)       | r₂     | 0.0109                 | 0.0045                 | 0.0014          | 0.0048  | 72.5    |
| Br₄ (C₂₋L₄)       | r₂     | 0.0113                 | 0.0047                 | 0.0014          | 0.0049  | 73.0    |
| Br₆ (C₂₋L₄)       | r₂     | 0.0119                 | 0.0049                 | 0.0014          | 0.0051  | 73.7    |
| Br₈ (C₂₋L₄)       | r₂     | 0.0114                 | 0.0047                 | 0.0014          | 0.0049  | 73.2    |
| Br₁₀ (C₂₋L₄)      | r₂     | 0.0124                 | 0.0050                 | 0.0014          | 0.0052  | 74.4    |
| Br₂ (C₂₋L₄)       | r₆     | 0.0120                 | 0.0049                 | 0.0014          | 0.0051  | 73.9    |
| Br₄ (C₂₋L₄)       | r₆     | 0.0114                 | 0.0047                 | 0.0014          | 0.0049  | 73.2    |
| Br₆ (C₂₋L₄)       | r₆     | 0.0125                 | 0.0051                 | 0.0014          | 0.0053  | 74.6    |
| Br₈ (C₂₋L₄)       | r₆     | 0.0120                 | 0.0051                 | 0.0014          | 0.0053  | 74.6    |
| Br₁₀ (C₂₋L₄)      | r₆     | 0.0126                 | 0.0051                 | 0.0014          | 0.0053  | 74.7    |
| Br₂ (C₂₋L₄)       | r₆     | 0.0127                 | 0.0051                 | 0.0014          | 0.0053  | 74.7    |
| Br₄ (C₂₋L₄)       | r₆     | 0.0126                 | 0.0051                 | 0.0014          | 0.0053  | 74.7    |
| Br₆ (C₂₋L₄)       | r₆     | 0.0120                 | 0.0049                 | 0.0014          | 0.0051  | 73.9    |
| Br₄ (C₂₋L₄)       | r₆     | 0.0104                 | 0.0044                 | 0.0014          | 0.0046  | 72.1    |
| Br₁₀ (C₂₋L₄)      | r₆     | 0.0118                 | 0.0048                 | 0.0014          | 0.0050  | 73.6    |
| Br₂ (C₂)           | r₂     | 0.0106                 | 0.0044                 | 0.0014          | 0.0046  | 72.3    |

### Table 2. The \( c_{ii} \), \( \theta_{p:CIV} \), \( \kappa_{p:CIV} \), and Predicted nature.

| Species (Symmetry) | \( c_{ii} \) (Å mdyn⁻¹) | \( \theta_{p:CIV} \) (°) | \( \kappa_{p:CIV} \) (au⁻¹) | Predicted nature |
|--------------------|--------------------------|------------------------|------------------------|----------------|
| Br₂ (C₂₋L₄)       | 15.311                   | 87.8                   | 121.2                  | p-CS/vdW 8     |
| Br₄ (C₂₋L₄)       | 14.984                   | 89.0                   | 124.9                  | p-CS/vdW 8     |
| Br₆ (C₂₋L₄)       | 14.114                   | 90.6                   | 127.3                  | p-CS/t-HB 9    |
| Br₈ (C₂₋L₄)       | 14.826                   | 89.2                   | 125.0                  | p-CS/vdW 8     |
| Br₁₀ (C₂₋L₄)      | 13.590                   | 92.2                   | 132.0                  | p-CS/t-HB 9    |
| Br₂ (C₂₋L₄)       | 14.048                   | 90.9                   | 127.1                  | p-CS/t-HB 9    |
| Br₄ (C₂₋L₄)       | 14.751                   | 89.4                   | 126.2                  | p-CS/vdW 8     |
| Br₆ (C₂₋L₄)       | 13.445                   | 92.6                   | 133.2                  | p-CS/t-HB 9    |
| Br₈ (C₂₋L₄)       | 13.478                   | 92.6                   | 132.5                  | p-CS/t-HB 9    |
| Br₁₀ (C₂₋L₄)      | 13.983                   | 92.6                   | 128.4                  | p-CS/IS-HB 9   |
| Br₂ (C₂₋L₄)       | 14.719                   | 92.7                   | 126.9                  | p-CS/vdW 8     |
| Br₄ (C₂₋L₄)       | 13.376                   | 93.0                   | 133.3                  | p-CS/t-HB 9    |
| Br₆ (C₂₋L₄)       | 13.334                   | 92.8                   | 132.6                  | p-CS/t-HB 9    |
| Br₈ (C₂₋L₄)       | 13.393                   | 92.8                   | 128.8                  | p-CS/IS-HB 9   |
| Br₁₀ (C₂₋L₄)      | 13.962                   | 91.1                   | 119.2                  | p-CS/vdW 8     |
| Br₂ (C₂)           | 16.025                   | 86.7                   | 119.2                  | p-CS/vdW 8     |
| Br₄ (C₂)           | 14.218                   | 90.2                   | 126.7                  | p-CS/vdW 8     |
| Br₆ (C₂)           | 16.378                   | 87.2                   | 120.0                  | p-CS/vdW 8     |

1 The interactions in minima are shown. 2 \( c\nabla^2\rho_b(r_c) = H_b(r_c) - V_b(r_c)/2 \), where \( c = \hbar^2/8m \). 3 \( R = (H_b(r_c) - V_b(r_c)/2)^2 + H_b(r_c)^2 \rangle^{1/2}. 4 \( \theta = 90° - \tan^{-1}[H_b(r_c)/(H_b(r_c) - V_b(r_c)/2)] \). 6 Defined in Equation (R1) in the text. 6 \( \kappa_p = \partial^2 y/\partial x^2 / [1 + (dy/\partial x)^2]^{3/2} \). 7 The pure CS interaction of the vdW nature. 9 The pure CS interaction of the HB nature without covalency.
Table 2. The $\rho_b(r_e)$, $H_b(r_e) − V_b(r_e)/2 = (h^2/8m)^2 \rho_b(r_e)$, and $H_b(r_e)$ values and QTAIM-DFA parameters for Br*-Br at BCPs in Br4–Br12, other than the C_s-L_m structures, evaluated with MP2/6-311+G(3df).

| Species      | BCP on | $\rho_b(r_e)$ | $\epsilon \nabla^2 \rho_b(r_e)^2$ | $H_b(r_e)$ | $R^3$ | $\theta^4$ |
|--------------|--------|---------------|----------------------------------|------------|-------|------------|
| (Symmetry)   | (au)   | (au)          | (au)                             | (au)       |       | (°)        |
| Br4 (C_{2s}) | r_{2}  | 0.0055        | 0.0022                           | 0.0009     | 0.0024| 67.2       |
| Br4 (D_{2d}) | r_{2}  | 0.0042        | 0.0017                           | 0.0007     | 0.0018| 66.0       |
| Br6 (C_{3v}-c) | r_{2}  | 0.0092        | 0.0038                           | 0.0013     | 0.0040| 70.7       |
| Br6 (S_{4})  | r_{2}  | 0.0128        | 0.0051                           | 0.0014     | 0.0053| 74.8       |
| Br_{8} (S_{4}-Wm) & 5 | r_{2}  | 0.0136        | 0.0054                           | 0.0013     | 0.0056| 76.0       |
| Br_{8} (S_{4}-Wm) & 5 | r_{3}  | 0.0038        | 0.0015                           | 0.0007     | 0.0016| 66.0       |
| Br_{10} (C_{2c}) | r_{2}  | 0.0087        | 0.0035                           | 0.0012     | 0.0037| 70.5       |
| Br_{10} (C_{2c}) | r_{4}  | 0.0097        | 0.0040                           | 0.0014     | 0.0042| 71.3       |
| Br_{10} (C_{2c}) | r_{6}  | 0.0110        | 0.0044                           | 0.0014     | 0.0046| 73.0       |
| Br_{10} (C_{2c}) | r_{7}  | 0.0049        | 0.0019                           | 0.0008     | 0.0021| 66.2       |
| Br_{10} (C_{2c}) | r_{8}  | 0.0049        | 0.0018                           | 0.0008     | 0.0020| 66.6       |
| Br_{12} (C_{1}) | r_{2}  | 0.0129        | 0.0052                           | 0.0014     | 0.0054| 75.0       |
| Br_{12} (C_{1}) | r_{4}  | 0.0129        | 0.0052                           | 0.0014     | 0.0054| 75.0       |

Species

| (Symmetry) | $C_{ii}$ | $\theta_{p:CIV}$ | $\kappa_{p:CIV}$ | Predicted nature |
|------------|----------|------------------|------------------|------------------|
| (au⁻¹)     | (°)      | (au⁻¹)           |                 |                  |
| Br4 (C_{2s}) | 24.709   | 73.6             | 122.9            | p-CS/vdW         |
| Br4 (D_{2d}) | 40.402   | 69.6             | 136.3            | p-CS/vdW         |
| Br6 (C_{3v}-c) | 25.617   | 83.3             | 121.7            | p-CS/vdW         |
| Br6 (S_{4})  | 13.201   | 93.5             | 139.2            | p-CS/-HB         |
| Br_{8} (S_{4}-Wm) & 5 | 11.294   | 95.3             | 139.0            | p-CS/-HB         |
| Br_{8} (S_{4}-Wm) & 5 | 52.918   | 67.5             | 204.0            | p-CS/vdW         |
| Br_{10} (C_{2c}) | 34.402   | 81.3             | 112.7            | p-CS/vdW         |
| Br_{10} (C_{2c}) | 23.971   | 84.7             | 122.1            | p-CS/vdW         |
| Br_{10} (C_{2c}) | 20.831   | 87.6             | 122.6            | p-CS/vdW         |
| Br_{10} (C_{2c}) | 29.570   | 71.5             | 118.9            | p-CS/vdW         |
| Br_{10} (C_{2c}) | 37.855   | 71.8             | 120.4            | p-CS/vdW         |
| Br_{12} (C_{1}) | 13.483   | 93.7             | 137.9            | p-CS/-HB         |
| Br_{12} (C_{1}) | 13.482   | 93.7             | 137.3            | p-CS/-HB         |

1 The interactions in minima are shown. 2 $\epsilon \nabla^2 \rho_b(r_e) = H_b(r_e) − V_b(r_e)/2$, where $\epsilon = h^2/8m$. 3 $R = [H_b(r_e) − V_b(r_e)/2]^2 + H_b(r_e)^2/2$. 4 $\theta = 90° − \tan^{-1}(H_b(r_e)/(H_b(r_e) − V_b(r_e)/2))$. 5 Image from windmill. 6 Defined in Equation (R1) in the text. 7 $\theta_p = 90° − \tan^{-1}(dy/dx)$, where $(x, y) = (H_b(r_e) − V_b(r_e)/2, H_b(r_e))$. 8 $\kappa_p = |d^2y/dx^2|/|1 + (dy/dx)^2|^{3/2}$. 9 The pure CS interaction of the vdW nature. 10 The pure CS interaction of the HB nature without covalency.

Figure 5. QTAIM-DFA plots ($H_b(r_e)$ versus $H_b(r_e) − V_b(r_e)/2$) for the interactions in Br_{10} (C_{2c}-L_{4}), evaluated with MP2/6-311+G(3df): (a) whole region, (b) pure CS region, and (c) SS region. Marks and colors are shown in the figure.
QTAIM-DFA parameters of \((R, \theta)\) and \((\theta_p, \kappa_p)\) are obtained by analyzing the plots of \(H_b(r_c)\) versus \(H_b(r_c) - V_b(r_c)/2\), according to Equations (S3)–(S6). Table 1 collects the QTAIM-DFA parameters for the noncovalent Br–Br interactions of Br4 \((C_s\text{-}L_1)–Br_{12} (C_s\text{-}L_5)\), Br6 \((C_2)\), and Br10 \((C_2)\) together with the \(C_{ii}\) values. Table 2 collects the \((R, \theta)\) and \((\theta_p, \kappa_p)\) values for Br4–Br12, other than those given in Table 1, together with the \(C_{ii}\) values. The \((R, \theta)\) and \((\theta_p, \kappa_p)\) values for the covalent Br–Br bonds in Br4–Br12 are collected in Table S4.

### 3.4. The Nature of Br–Br Interactions in Polybromine Clusters

The nature of the covalent and noncovalent Br–Br interactions in Br2–Br12 is discussed on the basis of the \((R, \theta, \theta_p)\) values, employing standard values as a reference (see Scheme SA3).

It is instructive to survey the criteria shown in Scheme SA3 before detailed discussion. The criteria tell us that \(180^\circ < \theta (H_b(r_c) - V_b(r_c)/2 < 0)\) for the SS interactions and \(\theta < 180^\circ (H_b(r_c) - V_b(r_c)/2 > 0)\) for the CS interactions. The CS interactions are subdivided into pure CS interactions \((p-CS)\) of \(45^\circ < \theta < 90^\circ (H_b(r_c) > 0)\) and regular CS interactions \((r-CS)\) of \(90^\circ < \theta < 180^\circ (H_b(r_c) < 0)\). The \(\theta_p\) 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 \(45^\circ < \theta_p < 90^\circ\) and the typical-HB type with no covalency \((t-HB_{nc})\) for \(90^\circ < \theta_p < 125^\circ\), where \(\theta_p = 125^\circ\) 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 \((R, \theta, \theta_p)\) values are \((0.0576\) au, \(184.3^\circ, 190.9^\circ)\) for the original Br2 if evaluated with MP2/6-311+G(3df). Therefore, the nature of the Br–Br bond in Br2 is classified by the SS interactions \((\theta > 180^\circ)\) and characterized to have a Cov-w nature \((\theta_p > 180^\circ\) and \(R < 0.15\) au). The nature is denoted by SS/Cov-w. The \((R, \theta, \theta_p)\) values for the covalent Br–Br bonds in Br4–Br12 are \((0.0472–0.0578\) au, \(182.0–184.4^\circ, 190.4–192.1^\circ)\); therefore, their nature is predicted to be SS/Cov-w. The nature of the covalent Br–Br bonds seems unchanged in the formation of the clusters \([53,54]\). The noncovalent Br–Br interactions in Br4–Br12 are all classified by pure CS interactions since \(\theta \leq 76^\circ (<< 90^\circ)\) \([53,54]\). The \(\theta_p\) values in the \(C_{s}\text{-}L_{m}\) clusters change systematically. The \(\theta_p\) values for \(r_2\) in Br2k \((C_{s}\text{-L}_{m}) (k=2–6)\) are predicted to be in the range of \(89.1^\circ \leq \theta_p \leq 89.6^\circ\), with \(\theta_p = 87.9^\circ\) for Br4 \((C_s\text{-}L_1)\).

However, the values for \(r_{n,2}\) in Br2k \((C_{s}\text{-L}_{m}) (k=2–6)\) are in the range of \(90.6^\circ \leq \theta_p \leq 91.2^\circ\) and the values for noncovalent interactions, other than edge positions, are in the range of \(92.1^\circ \leq \theta_p \leq 93.0^\circ\). Namely, the noncovalent Br–Br interactions are predicted to have the vdW nature \((p-CS/\text{vdW})\) for \(r_2\), while the interactions other than \(r_2\) are predicted to have the \(t-HB_{nc}\) nature \((p-CS/t-HB_{nc})\) since \(\theta_p > 90^\circ\). The \(\theta_p\) values of \(r_2\) for the \(C_{s}\text{-L}_{m}\) clusters will be less than \(90^\circ\), irrespective of the angles between \(r_1\) and \(r_2\), which are close to \(180^\circ\). The \(\theta_p\) values will be larger than \(90^\circ\) for all noncovalent interactions other than \(r_2\). Table 1 contains the data for Br10 \((C_2)\), of which \(\theta_p = 90.4^\circ\) \((>90^\circ)\) for \(r_2\) and \(\theta_p = 87.1^\circ\) \((<90^\circ)\) for \(r_4\), although Br10 \((C_2)\) is not the \(C_{s}\text{-L}_{m}\) 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 noncovalent Br–Br interactions in Br4–Br12, other than the \(C_{s}\text{-L}_{m}\) type clusters, \(\theta_p > 90^\circ\) for \(r_2\) in Br8 \((S_4) (\theta_p = 93.4^\circ)\) and Br8 \((S_4\text{-Wm}) (\theta_p = 94.8^\circ)\) and for \(r_2, r_4,\) and \(r_6\) in Br12 \((C_3) (93.4^\circ \leq \theta_p \leq 93.7^\circ)\). The interactions would have the \(t-HB_{nc}\) nature \((p-CS/t-HB_{nc})\). Very weak noncovalent Br–Br interactions are also detected. The ranges of \(64.2^\circ \leq \theta \leq 66.6^\circ\) and \(66.2^\circ \leq \theta_p \leq 71.2^\circ\) are predicted for \(r_2\) and \(r_3\) in Br4 \((C_{2h})\), \(r_2\) in Br4 \((C_{2v})\), \(r_3\) in Br4 \((S_4\text{-Wm})\), and \(r_7\) and \(r_8\) in Br10 \((C_{2\text{-C}})\). The results are summarized in Table 2.

What are the relationships between the QTAIM-DFA parameters for the noncovalent Br–Br interactions? The \(\theta\) and \(\theta_p\) values are plotted versus \(R\). The plots are shown in Figure S4; they give very good correlations. The \(\theta_p\) values are plotted versus \(\theta\). The plot is shown in Figure S5; it also gives a very good correlation. Table 3 summarizes the correlations among the QTAIM-DFA parameters.
Table 3. Correlations in the plots 1.

| Entry | Correlation | a     | b     | R^2  | n  |
|-------|-------------|-------|-------|------|----|
| 1     | ΔEZP vs. ΔEES | 0.940 | 0.129 | 0.9999 | 20  |
| 2     | \( \theta \) vs. R | 2595.6 | 60.70 | 0.979 | 33  |
| 3     | \( \theta_p \) vs. R | 6449.1 | 58.19 | 0.989 | 33  |
| 4     | \( \theta_p \) vs. \( \theta \) | 2.67 | -106.26 | 0.992 | 31  |
| 5     | \( E(2) \) vs. \( C_{ii}^{-1} \) | 535.5 | -18.22 | 0.997 | 15  |
| 6     | \( E(2) \) vs. \( R \) | 9760.9 | -29.92 | 0.983 | 15  |
| 7     | \( E(2) \) vs \( \theta \) | 2.446 | -160.88 | 0.996 | 15  |
| 8     | \( E(2) \) vs \( \theta_p \) | 1.067 | 77.17 | 0.999 | 15  |

1 The constants (a, b, R^2) are the correlation constant, the y-intercept, and the square of the correlation coefficient, respectively, in \( y = ax + b \). 2 Containing TS species. 3 Neglecting the data of \( r_2 \) and \( r_3 \) in Br4 (C2h). 4 For the noncovalent Br+-Br interactions in Br4 (C5v-L1)–Br12 (C5v-L5).

To further examine the behavior of noncovalent Br+-Br interactions, NBO analysis is applied to the interactions.

3.5. NBO Analysis for Br+-Br of Br4 (C5v-L1)–Br12 (C5v-L5)

The noncovalent Br+-Br interactions in Br4 (C5v-L1)–Br12 (C5v-L5) are characterized by \( \sigma(3c–4e) \) of the n(Br)→\( \sigma^*(Br–Br) \) type. NBO analysis [56] was applied to the n(Br)→\( \sigma^*(Br–Br) \) 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 Equation (4), where \( q_i \) is the donor orbital occupancy, \( \epsilon_i, \epsilon_j \) 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 \( n_i(\text{Br}) \)→\( \sigma^*(\text{Br–Br}) \) and \( n_p(\text{Br}) \)→\( \sigma^*(\text{Br–Br}) \), which are summarized in Table S5. The total values corresponding to \( n_i(\text{Br}) \)→\( \sigma^*(\text{Br–Br}) \) (+\( n_p(\text{Br}) \)→\( \sigma^*(\text{Br–Br}) \)) were calculated, which are also summarized in Table S5. The total values are employed for the discussion.

\[
E(2) = q_i \times F(i,j)^2 / (\epsilon_j - \epsilon_i)
\]

Figure 6 shows the plots of \( E(2) \) and \( \theta_p \) for the noncovalent Br+-Br interactions in Br4 (C5v-L1)–Br12 (C5v-L5). The values become larger in the order of \( C_{ii} \) for \( r_2 \) in Br4 (C5v-L1) < \( P(r_2; Br_6 (C_5v-L2)–Br_12 (C_5v-L5)) < P(r_2; Br_5 (C_5v-L2)–Br_12 (C_5v-L5)) \), where \( P \) means \( E(2) \) or \( \theta_p \), while \( r_\omega \) and \( r_n \) stand for the last end and the inside noncovalent 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 \( r_2 \) in Br4 (C5v-L1) < \( 17.7 \leq E(2) \leq 18.2 \) kJ mol\(^{-1} \) for \( r_2 \) in Br6 (C5v-L2)–Br12 (C5v-L5) < \( 19.5 \leq E(2) \leq 20.0 \) kJ mol\(^{-1} \) for \( r_\omega \) in Br6 (C5v-L2)–Br12 (C5v-L5) < \( 21.2 \leq E(2) \leq 22.0 \) kJ mol\(^{-1} \) for \( r_n \) in Br6 (C5v-L2)–Br12 (C5v-L5).

Relations between \( E(2) \) and \( C_{ii} \) were also examined for noncovalent Br+-Br interactions in Br4 (C5v-L1)–Br12 (C5v-L5). The \( E(2) \) values were plotted versus \( C_{ii}^{-1} \) for the noncovalent interactions. Figure 7 shows the plot. The plots give a very good correlation, which is shown in Table 3 (Entry 5). The results show that the energies for \( \sigma(3c–4e) \) of the \( n_p(\text{Br}) \)→\( \sigma^*(\text{Br–Br}) \) type in Br4 (C5v-L1)–Br12 (C5v-L5) are well evaluated, not only by \( E(2) \) but also by \( C_{ii}^{-1} \). Similar relations would be essentially observed for the interactions in the nonlinear 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 Br3 \( \sigma(3c–4e) \), the mutual interactions between Br3 \( \sigma(3c–4e) \), and/or the steric effect from other bonds and interactions, placed proximity in space. The \( E(2) \) values for Br4 (C5v-L1)–Br12 (C5v-L5) were also plotted versus \( R, \theta \), and \( \theta_p \), shown in Figures S6–S8, respectively. The plots give very good correlations, which are given in Table 3 (Entries 6–8).
3.6. MO Descriptions for Noncovalent Br---Br Interactions in Br₄

As discussed above, Br₃ σ(3c–4e) of the \( n_p(\text{Br}) \rightarrow \sigma^*(\text{Br}--\text{Br}) \) type plays an important role in the formation of Br₄ (C₅-L₁)–Br₁₂ (C₅-L₅). However, there must exist some interactions, other than Br₃ σ(3c–4e), to stabilize the clusters. The \( \Delta E_{ES} \) values for Br₄ (C₂h) (−8.0 kJ mol⁻¹) and Br₄ (D₂d) (−9.1 kJ mol⁻¹) are not so different from that for Br₄ (C₅-L₁) (−10.7 kJ mol⁻¹). However, Br₄ (C₂h) and Br₄ (D₂d) must consist of interactions other than...
σ(3c–4e). Indeed, Br₃ σ(3c–4e) of the n(Br)→σ*(Br–Br) type contributes to stabilizing Br₄ (C₅₋₁), but Br₄ (C₂₅) and Br₄ (D₂d) are shown to be stabilized by the σ(Br–Br)→σ*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 (Hᵣ(i)) over all electrons, Σᵢⁿ Hᵣ(i), and the electron–electron repulsive terms, (Σᵢ≠jn Jᵢj − Σᵢ≠jn Kᵢj)/2, as shown by Equation (5), where Hᵣ(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, εᵢ, over all electrons, Σᵢ=1ⁿ εᵢ, will be larger than E by (Σᵢ≠jn Jᵢj − Σᵢ≠jn Kᵢj)/2 since the electron–electron repulsions are doubly counted in Equation (6). Therefore, Σᵢⁿ Hᵣ(i) and (Σᵢ≠jn Jᵢj − Σᵢ≠jn Kᵢj)/2 are given separately by Equations (7) and (8), respectively.

(Σᵢ≠jn Jᵢj − Σᵢ≠jn Kᵢj)/2 = Σᵢ=1ⁿ εᵢ − E

The results show that Br₄ (C₅₋₁) is stabilized in the formation of the dimer from the components through the lowering of MO energies in total, in consistent with those evaluated with NBO, as discussed above.

Figure 8 shows the plots of ΔΣᵢⁿ Hᵣ(i) and Δ(Σᵢ≠jn Jᵢj − Σᵢ≠jn Kᵢj)/2 for Br₄ (C₅₋₁), Br₄ (C₂₅), and Br₄ (D₂d), together with ΔEₛₛ and ΔΣᵢ=1ⁿ εᵢ. In the case of Br₄ (C₅₋₁), ΔΣᵢⁿ Hᵣ(i) and Δ(Σᵢ≠jn Jᵢj − Σᵢ≠jn Kᵢj)/2 are evaluated to be 335.7 and −346.4 kJ mol⁻¹, respectively, which stabilizes Br₄ (C₅₋₁) in total. Two Br₂ molecules in Br₄ (C₅₋₁) will supply a wider area for electrons without severe disadvantageous steric compression by the L-shaped structure in a plane. The structural feature of Br₄ (C₅₋₁) may reduce (or may not severely increase) the electron–electron repulsive terms, Δ(Σᵢ≠jn Jᵢj − Σᵢ≠jn Kᵢj)/2, relative to the case of 2Br₂, although ΔΣᵢⁿ Hᵣ(i) seems to destabilize it. The ΔΣᵢⁿ Hᵣ(i) + Δ(Σᵢ≠jn Jᵢj − Σᵢ≠jn Kᵢj)/2 value is equal to −10.7 kJ mol⁻¹, which corresponds to the stabilization energy of Br₄ (C₅₋₁), relative to 2Br₂.
The energy profiles of Br$_4$ (C$_{2h}$) and Br$_4$ (D$_{2d}$) seem very different from that of Br$_4$ (Cs-L). The $\Delta\Sigma_i^{n\mu} \epsilon_i$ terms for Br$_4$ (C$_{2h}$) and Br$_4$ (D$_{2d}$) are evaluated to be 587.5 and 908.1 kJ mol$^{-1}$, respectively. Namely, Br$_4$ (C$_{2h}$) and Br$_4$ (D$_{2d}$) would be less stable than 2Br$_2$ if $\Delta\Sigma_i^{n\mu} \epsilon_i$ are compared. Consequently, it is difficult to explain the stability of Br$_4$ (C$_{2h}$) and Br$_4$ (D$_{2d}$), based on the MO energies. On the other hand, $\Delta\Sigma_i^{n\mu} H_c(i)$ of Br$_4$ (C$_{2h}$) and Br$_4$ (D$_{2d}$) are evaluated to be $-603.5$ and $-926.3$ kJ mol$^{-1}$, respectively, whereas $\Delta(\Sigma_i^{n\mu} J_{ij} - \Sigma_i^{(\neq j,\neq n)} K_{ij})/2$ are $595.5$ and $917.2$ kJ mol$^{-1}$, respectively. As a result, the $\Delta(\Sigma_i^{n\mu} H_c(i) + \Delta(\Sigma_i^{n\mu} J_{ij} - \Sigma_i^{(\neq j,\neq n)} K_{ij})/2)$ values are $-8.0$ and $-9.1$ kJ mol$^{-1}$ for Br$_4$ (C$_{2h}$) and Br$_4$ (D$_{2d}$), respectively, which correspond to their $\Delta E_{ES}$ values (relative to 2E(Br$_2$)). The results show that the stabilizing effect of $\Delta(\Sigma_i^{n\mu} H_c(i)$ overcomes the shorter electron–nuclear distances in the species on average. The shorter electron–electron distances must destabilize Br$_4$ (C$_{2h}$) and Br$_4$ (D$_{2d}$) through the factor of $\Delta(\Sigma_i^{n\mu} J_{ij} - \Sigma_i^{(\neq j,\neq n)} K_{ij})/2$, which is the inverse effect from the electron–nuclear interaction on $\Delta\Sigma_i^{n\mu} H_c(i)$. However, the effect of the shorter distances on $\Delta\Sigma_i^{n\mu} H_c(i)$ seems to contribute more effectively than the case of $\Delta(\Sigma_i^{n\mu} J_{ij} - \Sigma_i^{(\neq j,\neq n)} K_{ij})/2$ in Br$_4$ (C$_{2h}$) and Br$_4$ (D$_{2d}$), although they are not so large.

How can the BPs in Br$_4$ (C$_{2h}$) and Br$_4$ (D$_{2d}$) be rationalized through orbital interactions? The $\Delta\epsilon_i$ values of Br$_4$ (C$_{2h}$) are positive for all occupied MOs, relative to the corresponding values of 2Br$_2$, 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 to contribute well to stabilizing Br$_4$ (C$_{2h}$), but HOMO-4 (+40.8 kJ mol$^{-1}$) is also formed in the $\pi$(Br$_2$)-$\pi$(Br$_2$) mode. Similarly, HOMO (+13.7 kJ mol$^{-1}$) is formed, together with HOMO-3 in the $\pi^*(Br_2)$ + $\pi^*(Br_2)$ mode. Therefore, all MOs seem not to contribute to stabilizing Br$_4$ (C$_{2h}$) inherently. Nevertheless, HOMO, HOMO-4, and HOMO-7 seem to rationalize the appearance of BPs in Br$_4$ (C$_{2h}$), along the diagonal line and shorter sides of the parallelogram, although all electrons contribute to the appearance of BPs in molecules.
are –8.0 and –9.1 kJ mol–1 for Br4 (C2h) and Br4 (D2d), respectively, which correspond to their ΔE ES values (relative to 2E(Br2)). The results show that the stabilizing effect of ΔΣ in Hc (i) overcomes the shorter electron–nuclear distances in the species on average. The shorter electron–electron distances must destabilize Br4 (C2h) and Br4 (D2d) through the factor of Δ(Σi ≠ jn Jij − Σi ≠ j ‖n Kij)/2, which is the inverse effect from the electron–nuclear interaction on ΔΣ in Hc (i). However, the effect of the shorter distances on ΔΣ in Hc (i) seems to contribute more effectively than the case of Δ(Σi ≠ jn Jij − Σi ≠ j ‖n Kij)/2 in Br4 (C2h) and Br4 (D2d), although they are not so large.

How can the BPs in Br4 (C2h) and Br4 (D2d) be rationalized through orbital interactions?

The Δεi values of Br4 (C2h) are positive for all occupied MOs, relative to the corresponding values of 2Br2, 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 to contribute well to stabilizing Br4 (C2h), but HOMO-4 (+40.8 kJ mol–1) is also formed in the π(Br2)–π(Br2) mode. Similarly, HOMO (+13.7 kJ mol–1) is formed, together with HOMO-3 in the π*(Br2) + π*(Br2) mode. Therefore, all MOs seem not to contribute to stabilizing Br4 (C2h) inherently. Nevertheless, HOMO, HOMO-4, and HOMO-7 seem to rationalize the appearance of BPs in Br4 (C2h), along the diagonal line and shorter sides of the parallelogram, although all electrons contribute to the appearance of BPs in molecules.

Figure 9. Energy profile for the formation of Br4 (C2h), exemplified by HOMO, HOMO-3, HOMO-4, and HOMO-7.

Similarly, Δεi of Br4 (D2d) are positive for all occupied MOs, relative to the corresponding values of 2Br2, 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 Br4 (D2d). HOMO-4 (+50.2 kJ mol–1) is formed through the π(Br2)–π(Br2) mode in addition to HOMO-7. Similarly, HOMO (+13.9 kJ mol–1) is formed, accompanied by HOMO-3, in the π*(Br2) + π*(Br2) mode. Therefore, no MOs essentially stabilize Br4 (D2d). However, the appearance of BPs along the longer and shorter diagonal lines of the tetrahedron of Br4 (D2d) 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 is also of interest. Such investigations are in progress.

4. Conclusions

The intrinsic dynamic and static nature of noncovalent Br−−Br interactions was elucidated for Br4−Br10 with MP2/6-311+G(3df). QTAIM-DFA was applied to the investigation. $H_b(r_c)$ were plotted versus $H_b(r_c) - V_b(r_c)/2$ 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 Br4−Br10 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 noncovalent Br−−Br interactions in Br4−Br12 is classified by the pure CS interactions ($\theta \leq 76^\circ$). The noncovalent Br−−Br interactions in the linear type clusters of Br4 (Cs−L1)−Br12 (Cs−L5) are predicted to have the p-CS/t-HBnc nature ($90.6^\circ \leq \theta_p$), except for $r_2$, outside the ones of the first end, which have the p-CS/vdW nature, although it is very close to the border area between the two ($\theta_p \leq 89.4^\circ$). In the case of the cyclic clusters, the noncovalent Br−−Br interactions will have the p-CS/vdW nature ($\theta_p \leq 88.4^\circ$), except for $r_2$ in Br8 (S4) ($\theta_p = 93.5^\circ$) and Br8 (S4-Wm) ($\theta_p = 95.3^\circ$), which have the p-CS/t-HBnc nature.
The energies for Br$_3$ σ(3c–4e) of the $n_p$(Br)→σ*(Br–Br) type are well evaluated by not only $E(2)$ but also $C_{ii}^{-1}$ for Br$_4$ (C$_5$-L$_1$)–Br$_{12}$ (C$_5$-L$_5$). $E(2)$ correlates very well to $C_{ii}^{-1}$. The CT interactions of the $n_p$(Br)→σ*(Br–Br) type must contribute to form Br$_4$ (C$_5$-L$_1$), which can be explained based on the MO energies, $\epsilon_i$. However, it seems difficult to explain the stability of Br$_4$ (C$_5$H$_8$) and Br$_4$ (D$_{2d}$) based on the energies. The Br$_2$ molecules must be stacked more effectively in Br$_4$ (C$_5$H$_8$) and Br$_4$ (D$_{2d}$), resulting in shorter electronuclear distances on average. The energy lowering effect by ΔΣ$^m$ $H_i(i)$, due to the effective stacking of 2Br$_2$ in Br$_4$ (C$_5$H$_8$) and Br$_4$ (D$_{2d}$), contributes to form the clusters, although the inverse contribution from Δ((Σ$^m$)$^n$ $I_j^i$ – Σ$^m$̸$|$$^n$ $K_j^i$)/2) must also be considered.

**Supplementary Materials:** The following are available online, Table S1: Structural parameters for Br$_2$–Br$_{10}$, Table S2: Structural parameters for Br$_8$–Br$_{12}$, Table S3: The bond path distances and the straight-line distances in the polybromide clusters, together with the differences between the two, Table S4: The $\rho_5(r_c)$, $H_6(r_c) – V_5(r_c)/2 = (h^2/8m)\nabla^2 \rho_5(r_c)$, and $H_6(r_c)$ values and QTAIM-DFA parameters for Br$$\rightleftharpoons$$Br in polybromide clusters of Br$_2$–Br$_{12}$, Table S5: Contributions from the donor–acceptor (NBO(i)→NBO(j)) interactions of the n(Br)→σ*(Br–Br) type in the optimized structures of Br$_4$–Br$_{12}$, calculated using NBO analysis, Table S6: MO energies of Br$_3$ (C$_5$H$_8$), Table S7: MO energies of Br$_4$ (D$_{2d}$), Table S8: MO energies of Br$_2$ (D$_{oh}$), Table S9: MO energies of Br$_4$ (C$_5$-L$_1$), Table S10: The Δ$\epsilon$ values for Br$_4$ (C$_5$-L$_1$), relative to 2Br$_2$ (D$_{oh}$), Table S11: Energies for the Br$_4$ clusters and 2Br$_2$, together with the differences between the two, Figure S1: Plot of $\Delta E_ZP$ versus $\Delta E_{ES}$ for Br$_4$–Br$_{12}$, relative to those of Br$_2$, respectively, Figure S2: Plots of $\Delta E_{ES}$ for Br$_2$–Br$_{12}$ (C$_5$-L$_1$), Figure S3: Optimized structures for the cyclic bromine clusters of Br$_8$–Br$_{12}$, together with the linear type bromine cluster of Br$_{10}$, Figure S4: Plot of $\theta$ and $\theta_p$ versus $R$ for the noncovalent Br$$\rightleftharpoons$$Br interactions at the BCPs in the fully optimized structures of Br$_4$–Br$_{12}$, Figure S5: Plot of $\theta_p$ versus $\theta$ for the noncovalent Br$$\rightleftharpoons$$Br interactions at the BCPs in the fully optimized structures of Br$_4$–Br$_{12}$, Figure S6: Plot of $E(2)$ versus $R$ for noncovalent Br$$\rightleftharpoons$$Br interactions in Br$_4$ (C$_5$-L$_1$)–Br$_{12}$ (C$_5$-L$_5$), Figure S7: Plot of $E(2)$ versus $\theta$ for noncovalent Br$$\rightleftharpoons$$Br interactions in Br$_4$ (C$_5$-L$_1$)–Br$_{12}$ (C$_5$-L$_5$), Figure S8: Plot of $E(2)$ versus $\theta_p$ for noncovalent Br$$\rightleftharpoons$$Br interactions in Br$_4$ (C$_5$-L$_1$)–Br$_{12}$ (C$_5$-L$_5$), 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.

**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 $\rho_5(r_c)$, $H_6(r_c) – V_5(r_c)/2 = (h^2/8m)\nabla^2 \rho_5(r_c))$, and $H_6(r_c)$ values 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. All authors have read and agreed to the published version of the manuscript.

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**References and Notes**

1. Colin, J.J. Sur Quelques Combinaisons de l’iode. *Ann. Chim.* **1814**, *91*, 252–272.

2. Cavallo, G.; Metrangolo, P.; Pilati, T.; Resnati, G.; Terraneo, G. Halogen Bond: A Long Overlooked Interaction. In *Halogen Bonding I: Impact on Materials Chemistry and Life Sciences (Topics in Current Chemistry)*; Metrangolo, P., Resnati, G., Eds.; Springer: New York, NY, USA, 2015; Chapter 1; pp. 1–18.

3. Cavallo, G.; Metrangolo, P.; Milani, R.; Pilati, T.; Primagi, A.; Resnati, G.; Terraneo, G. The Halogen Bond. *Chem. Rev.* **2016**, *116*, 2478–2601. [CrossRef]

4. Bent, H.A. Structural chemistry of donor-acceptor interactions. *Chem. Rev.* **1968**, *68*, 587–648. [CrossRef]
5. Desiraju, G.R.; Parthasarathy, R. The nature of halogen halogen interactions: Are short halogen contacts due to specific attractive forces or due to close packing of nonspherical atoms? J. Am. Chem. Soc. 1989, 111, 8725–8726. [CrossRef]
6. Metrangolo, P.; Resnati, G. Halogen Bonding: A Paradigm in Supramolecular Chemistry. Chem. Eur. J. 2001, 7, 2511–2519. [CrossRef]
7. Erdélyi, M. Halogen bonding in solution. Chem. Soc. Rev. 2012, 41, 3547–3557. [CrossRef]
8. Beale, T.M.; Chudzinski, M.G.; Sarwar, M.G.; Taylor, M.S. Halogen bonding in solution: Thermodynamics and applications. Chem. Soc. Rev. 2013, 42, 1667–1680. [CrossRef] [PubMed]
9. Legon, A.C. Preparative Complexes of Dihalogen XY with Lewis Bases B in the Gas Phase: A Systematic Case for the Halogen Analogue B...XY of the Hydrogen Bond B XH. Angew. Chem. Int. Ed. 1999, 38, 2686–2714. [CrossRef]
10. Politzer, P.; Murray, J.S.; Clark, T. Halogen bonding and other σ-hole interactions: A perspective. Phys. Chem. Chem. Phys. 2013, 15, 11178–11189. [CrossRef]
11. Sugibayashi, Y.; Hayashi, S.; Nakanishi, W. Behavior of Halogen Bonds of the Y-X...Type (X, Y=F, Cl, Br, I) in the Benzene p System, Elucidated by Using a Quantum Theory of Atoms in Molecules Dual-Functional Analysis. Chem. Phys. Chem. 2016, 17, 2579–2589. [CrossRef] [PubMed]
12. Desiraju, G.R.; Ho, P.S.; Kloo, L.; Legon, A.C.; Marquardt, R.; Metrangolo, P.; Politzer, P.; Resnati, G.; Rissanen, K. Definition of the halogen bond (IUPAC Recommendations 2013). Pure Appl. Chem. 2013, 85, 1711–1713. [CrossRef]
13. Metrangolo, P.; Resnati, G. (Eds.) Halogen Bonding: Fundamentals and Applications; Series Structure and Bonding; Springer: New York, NY, USA, 2008.
14. Gierszal, K.P.; Davis, J.G.; Hands, M.D.; Wilcox, D.S.; Slipchenko, L.V.; Ben-Amotz, D. π-Hydrogen Bonding in Liquid Water. J. Phys. Chem. Lett. 2011, 2, 2930–2933. [CrossRef]
15. Categorizing Halogen Bonding and other Noncovalent Interactions Involving Halogen Atoms. A satellite event of the XXII Congress and General Assembly of the International Union of Crystallography, 2010; https://doi.org/10.1515/ci.2010.32.2.20 (accessed on 1 May 2021).
16. Donohue, J.; Goodman, S.H. Interatomic distances in solid chlorine. Acta Cryst. 1965, 18, 568–569. [CrossRef]
17. Powell, B.M.; Heal, K.M.; Torrie, B.H. The temperature dependence of the crystal structures of the solid halogens, bromine and chlorine. Mol. Phys. 1984, 53, 929. [CrossRef]
18. Van Bolhuis, F.; Koster, P.B.; Migchelsen, T. Refinement of the crystal structure of iodine at 110° K. Acta Cryst. 1967, 23, 90–91. [CrossRef]
19. Schuster, P.; Mikosch, H.; Bauer, G. All electron density functional study of neutral and ionic polybromine clusters. J. Chem. Phys. 1998, 109, 1833–1844. [CrossRef]
20. Sung, D.; Park, N.; Park, W.; Hong, S. Formation of polybromine anions and concurrent heavy hole doping in carbon nanotubes. Appl. Phys. Lett. 2007, 90, 093502. [CrossRef]
21. Nakanishi, W.; Hayashi, S.; Narahara, K. Polar Coordinate Representation of Hθ(rθ) versus (h2/8m)(∇2ρθ)(rθ) at BCP in AIM Analysis: Classification and Evaluation of Weak to Strong Interactions. J. Phys. Chem. A 2009, 113, 10050–10057. [CrossRef]
22. Nakanishi, W.; Hayashi, S. Atoms-in-Molecules Dual Functional Analysis of Weak to Strong Interactions. Curr. Org. Chem. 2010, 14, 181–197. [CrossRef]
23. Nakanishi, W.; Hayashi, S. Dynamic Behaviors of Interactions: Application of Normal Coordinates of Internal Vibrations to AIM Dual Functional Analysis. J. Phys. Chem. A 2010, 114, 7423–7430. [CrossRef]
24. Nakanishi, W.; Hayashi, S.; Matsuiwa, K.; Kitamoto, M. Applications of Normal Coordinates of Internal Vibrations to Generate Perturbed Structures: Dynamic Behavior of Weak to Strong Interactions Elucidated by Atoms-in-Molecules Dual Functional Analysis. Bull. Chem. Soc. Jpn. 2012, 85, 1293–1305. [CrossRef]
25. Nakanishi, W.; Hayashi, S. Role of dG/dw and dV/dw in AIM Analysis: An Approach to the Nature of Weak to Strong Interactions. J. Phys. Chem. A 2013, 117, 1795–1803. [CrossRef] [PubMed]
26. Bader, R.F.W. Atoms in Molecules: A Quantum Theory; Oxford University Press: Oxford, UK, 1990.
27. Matta, C.F.; Boyd, R.J. An Introduction to the Quantum Theory of Atoms in Molecules. In The Quantum Theory of Atoms in Molecules: From Solid State to DNA and Drug Design; WILEY-VCH: Weinheim, Germany, 2007.
28. Nakanishi, W.; Hayashi, S.; Nishide, T. Intrinsic dynamic and static nature of each HB in the multi-HBs between nucleobase pairs and its behavior, elucidated with QTAIM dual functional analysis and QC calculations. RSC Adv. 2020, 10, 24730–24742. [CrossRef]
29. See also Figure 5 for the definition of (R, θ) and (θ∂p, κp), exemplified by the rθ in Br2I6 (Cv-L5).
30. Nakanishi, W.; Hayashi, S. Perturbed structures generated using coordinates derived from compliance constants in internal vibrations for QTAIM dual functional analysis: Intrinsic dynamic nature of interactions. Int. J. Quantum Chem. 2018, 118, e25590–e25591. [CrossRef]
31. The basic concept for the compliance constants was introduced by Taylor and Pitzer, followed by Konkoli and Cremer.
32. Taylor, W.T.; Pitzer, K.S. Vibrational frequencies of semirigid molecules: A general method and values for ethylbenzene. J. Res. Natl. Bur. Stand. 1947, 38, 1–17. [CrossRef]
33. Konkoli, Z.; Cremer, D. A new way of analyzing vibrational spectra. I. Derivation of adiabatic internal modes. Int. J. Quantum Chem. 1998, 67, 1–9. [CrossRef]
34. The $C_{ij}$ are defined as the partial second derivatives of the potential energy due to an external force, as shown in Equations (R1), 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.

\[ C_{ij} = \frac{\partial^2 E}{\partial f_i \partial f_j} \]  

(R1).

35. 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. Available online: http://www.oc.tu-bs.de/Grunenberg/compliance.html (accessed on 1 May 2021).

36. Brandhorst, K.; Grunenberg, J. Efficient computation of compliance matrices in redundant internal coordinates from Cartesian Hessians for nonstationary points. J. Chem. Phys. 2010, 132, 184101. [CrossRef]

37. Brandhorst, K.; Grunenberg, J. How strong is it? The interpretation of force and compliance constants as bond strength descriptors. Chem. Soc. Rev. 2008, 37, 1558–1567. [CrossRef] [PubMed]

38. Brandhorst, K.; Grunenberg, J. III-defined concepts in chemistry: Rigid force constants vs. compliance constants as bond strength descriptors for the triple bond in diboryne. Chem. Sci. 2015, 6, 4086–4088. [CrossRef] [PubMed]

39. Frisch, M.J.; Trucks, G.W.; Schlegel, H.B.; Scuseria, G.E.; Robb, M.A.; Cheeseman, J.R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G.A.; et al. Gaussian 09 (Revision D.01), Gaussian, Inc.: Wallingford, CT, USA, 2009.

40. Gauss, J. Accurate Calculation of NMR Chemical Shifts. Ber. Bunsen-Ges. Phys. Chem. 1995, 99, 1001–1008. [CrossRef]

41. Gauss, J. Effects of electron correlation in the calculation of nuclear magnetic resonance chemical shifts. J. Chem. Phys. 1993, 99, 3629–3643. [CrossRef]

42. Curtiss, L.A.; McGrath, M.P.; Blaudeau, J.-P.; Davis, N.E.; Binning, R.C., Jr.; Radom, L. Extension of Gaussian-2 theory to molecules containing third-row atoms Ga–Kr. J. Chem. Phys. 1995, 103, 6104–6113. [CrossRef] [PubMed]

43. Curtiss, L.A.; McGrath, M.P.; Blaudeau, J.-P.; Davis, N.E.; Binning, R.C., Jr.; Radom, L. Efficient diffuse function-augmented basis sets for anion calculations. J. Comput. Chem. 2000, 21, 1040–1048. [CrossRef]

44. Clark, T.; Chandrasekhar, J.; Spitznagel, G.W.; Schleyer, P.v.R. Efficient diffuse function-augmented basis sets for anion calculations. III. The 3-21+G basis set for first-row elements, Li–F. J. Chem. Soc. Rev. 1991, 94, 511–516. [CrossRef]

45. McGrath, M.P.; Pletzer, M.S. Note on an Approximation Treatment for Many-Electron Systems. Phys. Rev. 1934, 46, 618–622. [CrossRef]

46. Binning, R.C.; Curtiss, L.A. Compact contracted basis sets for third-row atoms: Ga–Kr. J. Comput. Chem. 1990, 11, 1206–1216. [CrossRef]

47. Binning, R.C.; Curtiss, L.A. Calculation of atomic integration data. J. Comput. Chem. 2000, 21, 1040–1048. [CrossRef]

48. Biegler-König, F.; Schönbohm, J. The AIM2000 Program (Version 2.0). Available online: http://www.aim2000.de (accessed on 1 May 2021).

49. Gauss, J. The 3-21+G basis set for first-row elements, Li–F. J. Chem. Phys. 1983, 83, 294–301. [CrossRef]

50. Møller, C.; Plesset, M.S. Note on an Approximation Treatment for Many-Electron Systems. Phys. Rev. 1934, 46, 618–622. [CrossRef]

51. Frisch, M.J.; Trucks, G.W.; Schlegel, H.B.; Scuseria, G.E.; Robb, M.A.; Cheeseman, J.R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G.A.; et al. Gaussian 09 (Revision D.01), Gaussian, Inc.: Wallingford, CT, USA, 2009.

52. Biegler-König, F.; Schönbohm, J. Calculation of atomic integration data. J. Comput. Chem. 2000, 21, 1040–1048. [CrossRef]

53. Keith, T.A. AIMAll (Version 17.11.14), TK Gristmill Software, Overland Park KS, USA. 2017. Available online: http://aim.tkgristmill.com (accessed on 1 May 2021).

54. Curtiss, L.A.; McGrath, M.P.; Blaudeau, J.-P.; Davis, N.E.; Binning, R.C., Jr.; Radom, L. Extension of Gaussian-2 theory to molecules containing third-row atoms Ga–Kr. J. Chem. Phys. 1995, 103, 6104–6113. [CrossRef] [PubMed]

55. Biegler-König, F.; Schönbohm, J. The AIM2000 Program (Version 2.0). Available online: http://www.aim2000.de (accessed on 1 May 2021).

56. Frisch, M.J.; Trucks, G.W.; Schlegel, H.B.; Scuseria, G.E.; Robb, M.A.; Cheeseman, J.R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G.A.; et al. Gaussian 09 (Revision D.01), Gaussian, Inc.: Wallingford, CT, USA, 2009.

57. Biegler-König, F.; Schönbohm, J. Efficient computation of compliance matrices in redundant internal coordinates from Cartesian Hessians for nonstationary points. J. Chem. Phys. 2010, 132, 184101. [CrossRef]