Noncovalent interactions between benzochalcogenadiazoles and nitrogen bases

Lili Zhang1 · Yanli Zeng1 · Xiaoyan Li1 · Xueying Zhang1

Received: 21 June 2022 / Accepted: 25 July 2022 / Published online: 6 August 2022
© The Author(s), under exclusive licence to Springer-Verlag GmbH Germany, part of Springer Nature 2022

Abstract
A theoretical study has been carried out on the intermolecular interactions between tetrafluoro-benzochalcogenadiazoles (chalcogen = S, Se, Te) and a series of nitrogen bases (FCN, CICN, NP, trans-N2H2, pyridine, pyrazole, imidazole) at the B97-D3/def2-TZVP level, to obtain a better insight into the nature and strength of Ch···N chalcogen bond and secondary interaction in the binary and 1:2 ternary complexes. The dispersion force plays a prominent role on the stability of the sulfur complexes, and the electrostatic effect enhanced for the heavier chalcogen complexes. Most of intermolecular bonds display the characters of closed-shell and noncovalent interaction. For the complexes involving pyridine and imidazole, chalcogen bond is stronger than hydrogen bond, while the strength of chalcogen bond is equivalent to the secondary interaction for other complexes. With the addition of nitrogen base in the 1:2 complexes, chalcogen bond is weakened, while the secondary interaction remains unchanged. In the 1:2 complexes formed by pyridine and imidazole, stronger chalcogen bond results in larger negative cooperativity than that of other complexes.

Keywords Noncovalent interaction · Chalcogen bond · Topological analysis · Benzochalcogenadiazoles

Introduction
Noncovalent interaction exists in many chemical, biological, and functional systems and plays an important role in supramolecular chemistry, crystal engineering, biology, and catalysis [1, 2]. Noncovalent interactions cover all main groups of the Periodic Table, including hydrogen bond (HB), tetrel bond, chalcogen bond, halogen bond, and so on [3–6]. The chalcogen bond (ChB) was defined [7] as an attractive interaction between an electrophilic region associated with a chalcogen atom in a molecular entity and a nucleophilic region in another, or the same, molecular entity. The chalcogen atom, such as S, Se, and Te, is characterized by the region of positive electrostatic potential, which is designated as σ-hole or π-hole [8–12]. Chalcogen bond shares more similarities with hydrogen and halogen bonds, while there are several specific features, such as directionality, tunability, hydrophobicity, donor atom size, and multiplicity [13]. It can be used as a driving force toward desired selectivity in the design of materials, molecular recognition, and self-assembly and play a crucial role in organic synthesis and noncovalent organocatalysis [14–18].

In recent years, chalcogen-nitrogen π heterocycles, such as 1,2,5-chalcogenadiazoles, 1,2,3-dithiazoles, and their Se/Te analogues, attracted more attention due to their biological relevance and the ability to form supermolecular synths [15, 16, 19–36]. Chalcogen in these compounds, particularly in the tellurium-bearing congeners, acts as a monodentate or bidentate ChB donor, is prone to association in the solid state through Cha···N interaction [19, 20]. The self-association of chalcogenadiazoles and benztelluradiazoles could lead to stabilized chains, ribbons, cyclic aggregates, or supramolecular capsules [21–25]. Bryce’s studies [26] revealed that dicyanoselenadiazole and dicyanotelluradiazole derivatives work as promising supramolecular synths with the ability to form double chalcogen bonds with a wide range of electron donors including halides and oxygen- and nitrogen-containing heterocycles. Fourmigué et al. [27] demonstrated that the combination of tellurium activation through alkynyl substitution provides
an efficient template for the successful construction of robust molecular rectangles. The strength of certain ChB's is strong enough that it persists in solution. Donor–acceptor complexes between 1,2,5-chalcogenadiazoles and anionic (Cl\(^{-}\), Br\(^{-}\), I\(^{-}\), CN\(^{-}\), XCN\(^{-}\)) [28, 29] in organic solvent were studied using UV/Vis and NMR spectroscopies, and DFT calculations. Vargas-Baca and coworkers [30, 31] reported the results of laser desorption/ionization time-of-flight mass spectrometry experiments performed on several benzo-2,1,3-chalcogenadiazoles and provided the evidence of the persistence of Te···N supramolecular association in the gas phase and in solution. The origin of the attractions in chalcogen-nitrogen interactions is important for understanding the nature of these interactions. Electrostatic and dispersion interactions are the major sources of the attraction in the 1,2,5-chalcogenadiazole dimers [32]. Steric interactions [33] is important in conformational control of strong chalcogen bonds in tellurium-containing aromatics. The structures and properties of the chalcogenadiazole homodimer or heterodimer were explored by quantum chemical calculations [34–36]. Scheiner [36] analyzed the influence of the ring size and the number of N atoms within the diazole ring on the strengths of the 2Ch···2N square bonding.

In the present work, we focused on the detailed theoretical studies on the intermolecular interactions between tetrafluoro-benzochalcogenadiazoles (chalcogen = S, Se, Te) and a series of nitrogen bases, including the sp-hybridized bases (FCN, CICN, NP) and sp\(^{2}\)-hybridized bases (trans-N\(_{2}\)H\(_{2}\), pyridine, pyrazole, imidazole). The purposes are the following: First, determine the strength of intermolecular interactions and nature of intermolecular bonding. Second, insight into the main factor that controls the intermolecular interaction; and figure out the difference between sulfur atom and heavier chalcogen atoms. It has been demonstrated that no evidence was obtained for the formation of 1:2 complexes with Cl\(^{-}\) or other anions in solution [28]. What about the 1:2 complexes with neutral N-bases in gas? So, the third

\[\text{Fig. 1} \quad \text{MEP diagrams for benzochalcogenadiazoles and N-bases}\]
Fig. 2  Optimized geometries of the binary complexes
Computational methods

The geometries of the monomers and the complexes were optimized and characterized in the light of frequency computations with the Gaussian09 program [37]. Geometries were fully optimized with the dispersion-corrected B97-D3 functional and the def2-TZVP basis set. This method has been proved to give good agreement with the experimental free energies of ChB interactions involving benzotelluradiazoles [28, 29]. The binding energies were evaluated as the difference in energy between the complex and the sum of the isolated optimized monomers, which include the zero point vibrational energy (ZPVE) and basis set superposition error (BSSE) [38] corrections. The energy decomposition analysis was performed by the GAMESS program [39] with the localized molecular orbital energy decomposition analysis (LMOEDA) method [40] at the B97-D3/def2-TZVP level. The molecular electrostatic potentials (MEPs) of monomers and complexes were calculated on the 0.001 a.u. contour of density surface with the WFA-SAS program [41]. The topological properties of electron density at the bond critical points (BCPs) were obtained using the AIMAll program [42]. The Multiwfn program [43] and VMD program [44] were used to calculate and plot the map of noncovalent interaction (NCI) index, and molecule formation density difference (MFDD).

Results and discussion

Geometries and binding energies of the binary complexes

As a preliminary gauge of intermolecular interaction, MEPs analyses of monomers were performed. From Fig. 1, tetrafluoro-benzotelluradiazole exhibits two “σ-holes” [9, 10] regions of electron deficiency centered at the tellurium atom, situated roughly at the terminus of a Te–N bond. The most positive MEP values ($V_{s,max}$) of benzochalcogenadiazoles

| Complex | $d$(Ch···N3) | $\Delta d$(Ch···N3) | $d$(H···N2) | $\Delta d$(H···N2) | $\angle$N1ChN3 | $\Delta E$ (kJ/mol) |
|---------|--------------|------------------|--------------|------------------|----------------|-----------------|
| 1···NCF | 3.372        | 0.022            | -            | -                | 176            | -12.1           |
| 1···NCCI | 3.353      | 0.003            | -            | -                | 179            | -12.4           |
| 1···NP | 3.425        | 0.075            | -            | -                | 178            | -12.6           |
| 1···N$_2$H$_2$ | 3.076 | -0.274           | 2.313        | -0.437           | 175            | -16.4           |
| 1···C$_{6}$NH$_5$ | 2.980 | -0.370           | 2.631        | -0.119           | 179            | -17.7           |
| 1···m-C$_3$N$_2$H$_4-a$ | 3.020 | -0.323           | 2.650        | -0.100           | 180            | -19.2           |
| 1···m-C$_3$N$_2$H$_4-b$ | 3.028 | -0.322           | 2.707        | -0.043           | 179            | -16.7           |
| 1···o-C$_3$N$_2$H$_4-a$ | 3.075 | -0.275           | 2.195        | -0.555           | 177            | -26.7           |
| 1···o-C$_3$N$_2$H$_4-b$ | 3.106 | -0.244           | 2.703        | -0.047           | 179            | -14.0           |
| 2···NCF | 3.312        | -0.138           | -            | -                | 168            | -16.2           |
| 2···NCCI | 3.289      | -0.161           | -            | -                | 172            | -16.7           |
| 2···NP | 3.320        | -0.130           | -            | -                | 173            | -17.8           |
| 2···N$_2$H$_2$ | 2.953 | -0.497           | 2.255        | -0.495           | 168            | -24.1           |
| 2···C$_{6}$NH$_5$ | 2.820 | -0.631           | 2.577        | -0.173           | 174            | -28.3           |
| 2···m-C$_3$N$_2$H$_4-a$ | 2.856 | -0.594           | 2.616        | -0.134           | 173            | -30.1           |
| 2···m-C$_3$N$_2$H$_4-b$ | 2.865 | -0.585           | 2.667        | -0.083           | 174            | -26.8           |
| 2···o-C$_3$N$_2$H$_4-a$ | 2.909 | -0.541           | 2.148        | -0.602           | 171            | -37.6           |
| 2···o-C$_3$N$_2$H$_4-b$ | 2.965 | -0.485           | 2.678        | -0.072           | 173            | -21.4           |
| 3···NCF | 3.271        | -0.339           | -            | -                | 159            | -21.7           |
| 3···NCCI | 3.227      | -0.383           | -            | -                | 162            | -23.2           |
| 3···NP | 3.181        | -0.429           | -            | -                | 162            | -26.6           |
| 3···N$_2$H$_2$ | 2.831 | -0.779           | 2.159        | -0.591           | 159            | -37.6           |
| 3···C$_{6}$NH$_5$ | 2.756 | -0.854           | 2.482        | -0.268           | 165            | -45.2           |
| 3···m-C$_3$N$_2$H$_4-a$ | 2.735 | -0.875           | 2.549        | -0.201           | 164            | -48.7           |
| 3···m-C$_3$N$_2$H$_4-b$ | 2.749 | -0.861           | 2.594        | -0.156           | 164            | -44.1           |
| 3···o-C$_3$N$_2$H$_4-a$ | 2.760 | -0.850           | 2.062        | -0.688           | 161            | -56.9           |
| 3···o-C$_3$N$_2$H$_4-b$ | 2.816 | -0.794           | 2.626        | -0.124           | 163            | -34.7           |
are 22.0, 28.7, and 36.8 kcal/mol for Ch = S, Se, and Te, respectively. The more polarizable and less electronegative the chalcogen is, the larger $V_{\text{max}}$ value, the greater the tendency of that chalcogen is to form close contacts with Lewis base. For sp-hybridized nitrogen bases (FCN, ClCN), negative and positive MEP are located on N atom and π-hole [12, 45] above C atom. For sp$^2$-hybridized nitrogen bases ($\text{trans-N}_2\text{H}_2$, $\text{C}_2\text{N}_2\text{H}_4$, $\text{m-C}_3\text{N}_2\text{H}_4$, $\text{o-C}_3\text{N}_2\text{H}_4$), N and H atoms act as nucleophilic and electrophilic sites.

Figure 2 shows the optimized geometries of the tellurium complexes; the sulfur and selenium ones are analogous. In this paper, symbols 1, 2, and 3 were used for representing tetrafluoro-benzochalcogenadiazoles, which correspond to Ch = S, Se, and Te. The difference of type-a and type-b in the complexes is different interacting H atom of imidazole and pyrazole. Table 1 gives the binding energies, main geometrical parameters, and their variations in the binary complexes, in which $\Delta d(\text{Ch} \cdots \text{N3})$ and $\Delta d(\text{H} \cdots \text{N2})$ indicate the difference between binding distances Ch···N3, H···N2 and the sum of the corresponding van der Waals radii [46] ($r_{\text{vdw}}(\text{S})=1.80\text{Å}$, $r_{\text{vdw}}(\text{Se})=1.90\text{Å}$, $r_{\text{vdw}}(\text{Te})=2.06\text{Å}$, $r_{\text{vdw}}(\text{N})=1.55\text{Å}$, $r_{\text{vdw}}(\text{H})=1.20\text{Å}$). For the same nitrogen base, the values of $\Delta d(\text{Ch} \cdots \text{N3})$ and $\Delta d(\text{H} \cdots \text{N2})$ become more negative from Ch = S to Se and Te, indicating more strong interaction occurs. For the same benzochalcogenadiazole, sp$^2$ hybrid nitrogen bases have much larger variations than those for sp hybrid nitrogen bases.

From Table 1, the binding energies are in the range from $-12.1 \text{kJ/mol}$ for 1···NCF to $-56.9 \text{kJ/mol}$ for 3···$\text{o-C}_3\text{N}_2\text{H}_4$-a. For the same nitrogen base, the binding energy becomes more negative in the sequence Ch = S < Se < Te. For the same benzochalcogenadiazole, the strength of intermolecular interaction increases with the order of FCN < ClCN < NP < $\text{N}_2\text{H}_2$ < $\text{C}_2\text{N}_2\text{H}_4$ < $\text{m-C}_3\text{N}_2\text{H}_4$-a < $\text{o-C}_3\text{N}_2\text{H}_4$-a. For the complexes with $\text{C}_3\text{N}_2\text{H}_4$, the binding energy of type-a is more negative than that of type-b.

**NCI analyses**

Noncovalent interaction (NCI) analysis [47, 48] provides an index, based on the electron density ($\rho$) and its reduced gradient ($s$), and the information for van der Waals interactions,
hydrogen bonds, and steric repulsion. This index visualizes the extent to which NCIs stabilize a supramolecular assembly qualitatively and reveals which molecular regions interact. The scatter diagram of reduced density gradient (RDG) versus the electron density multiplied by the sign of the second Hessian eigenvalue \((\text{sign}(\lambda_2)\rho)\) and plots of gradient isosurfaces were generated and shown in Fig. 3. A large irregular area with different colors is found between both molecules, indicative of the coexistence of more than one interaction. For example, there are two near spikes in the low-density, low-gradient trough \((\text{sign}(\lambda_2)\rho < -0.013\text{ a.u.})\) in the 3···NCCl complex, corresponding green regions shown in the gradient isosurfaces, which is indicative of the weak attractive interaction between them. In the complexes 3···C3N2 H4; the intermolecular region is marked by one bluish and one green isosurface, which corresponding to the moderate Te···N3 chalcogen bond and the weak H···N hydrogen bond, respectively.

**QTAIM analyses**

According to the Bader’s QTAIM [49, 50], the topological properties at the critical points are vital criteria to be considered when discussing the strength and nature of a chemical bond. The molecular graphs of representative complexes 3···N-bases are displayed in Fig. 4, the properties at the intermolecular bond critical points (BCPs) are calculated and listed in Table 2. There are two BCPs and one ring critical point (RCP) in the complexes; chalcogen bond is evidenced by the presence of Te···N3 BCP and a pair of bond path between Te and N3 atoms. In the complexes containing sp-hybridized nitrogen bases, bond paths connecting N2-atom to the C or P-atom of nitrogen base correspond to a π-hole or pnicogen bond. In the complexes containing sp2-hybridized nitrogen bases, hydrogen bond is evidenced by the presence of N2···H BCP and corresponding bond paths. The result is in agreement with the conclusion which is drawn from NCI analyses.

The strength of the bond between two nuclei could be predicted from the electron density \((\rho_b)\) [49] and potential energy density \((V_b)\) [51, 52] at the BCP that characterize the interaction. From Table 2, for the complexes formed by C3NH5 and m-C3N2H4, the values of \(\rho_b\) and \(V_b\) at the BCP of Ch···N3 contact are larger than those of N2···H contact, indicating the strength of ChB is stronger than that of HB. For other complexes, the \(\rho_b\) and \(V_b\) values at the

---

**Fig. 4** Molecular graphs of the representative binary complexes
intermolecular BCPs are generally approaches, indicating the strength of ChB is close to the secondary interaction. In addition, the sign of $\nabla^2 \rho_b$ and total energy density ($H_b$) at the BCP provides further information regarding the nature of the interaction \cite{50, 53}. $\nabla^2 \rho_b > 0$ and $H_b > 0$ indicate a closed-shell interaction, whereas $\nabla^2 \rho_b < 0$ and $H_b < 0$ are indicative of a covalent bond. It has also been claimed that if $\nabla^2 \rho_b > 0$, $H_b < 0$ and $0.5 < -G_b/V_b < 1$, the interaction is partly covalent in nature. From Table 2, positive $\nabla^2 \rho_b$ values, negative $H_b$ values, and $-G_b/V_b$ values of about 0.9 were calculated for the Te···N3 BCPs in the complexes involving sp$^2$-hybridized N-bases, indicative of a partially covalent nature of the corresponding chalcogen bonds. For other BCPs, both $\nabla^2 \rho_b$ and $H_b$ were positive, and $-G_b/V_b$

Table 2: Topological properties at the intermolecular BCPs for the binary complexes (all values are in a.u.)

| Complex | BCP | $\rho_b$ | $\nabla^2 \rho_b$ | $G_b$ | $V_b$ | $H_b$ | $-G_b/V_b$ |
|---------|-----|---------|-----------------|------|------|-------|------------|
| 1···NCF | N2···C | 0.009 | 0.030 | 0.006 | -0.005 | 0.001 | 1.283 |
| 1···NCCI | S···N3 | 0.006 | 0.021 | 0.004 | -0.003 | 0.001 | 1.519 |
| N2···C | 0.007 | 0.024 | 0.005 | -0.004 | 0.001 | 1.360 |
| 1···NP | S···N3 | 0.005 | 0.019 | 0.004 | -0.002 | 0.001 | 1.534 |
| N2···P | 0.008 | 0.023 | 0.005 | -0.004 | 0.001 | 1.288 |
| 1···N$_2$H$_2$ | S···N3 | 0.012 | 0.036 | 0.008 | -0.006 | 0.001 | 1.230 |
| N2···H | 0.014 | 0.047 | 0.010 | -0.008 | 0.002 | 1.241 |
| 1···C$_2$NH$_4$ | S···N3 | 0.015 | 0.043 | 0.009 | -0.008 | 0.001 | 1.168 |
| N2···H | 0.008 | 0.029 | 0.006 | -0.004 | 0.002 | 1.346 |
| 1···m-C$_2$N$_2$H$_5$ | S···N3 | 0.013 | 0.040 | 0.009 | -0.007 | 0.002 | 1.211 |
| N2···H | 0.008 | 0.029 | 0.006 | -0.004 | 0.002 | 1.360 |
| 1···o-C$_2$N$_2$H$_5$ | S···N3 | 0.012 | 0.037 | 0.008 | -0.006 | 0.002 | 1.241 |
| N2···H | 0.017 | 0.061 | 0.013 | -0.010 | 0.003 | 1.243 |
| 2···NCF | Se···N3 | 0.007 | 0.025 | 0.005 | -0.003 | 0.001 | 1.408 |
| N2···C | 0.009 | 0.032 | 0.007 | -0.005 | 0.001 | 1.267 |
| 2···NCCI | Se···N3 | 0.007 | 0.025 | 0.005 | -0.004 | 0.001 | 1.389 |
| N2···C | 0.007 | 0.026 | 0.005 | -0.004 | 0.001 | 1.341 |
| 2···NP | Se···N3 | 0.007 | 0.025 | 0.005 | -0.003 | 0.001 | 1.408 |
| N2···P | 0.009 | 0.026 | 0.005 | -0.004 | 0.001 | 1.262 |
| 2···N$_2$H$_2$ | Se···N3 | 0.017 | 0.045 | 0.010 | -0.009 | 0.001 | 1.113 |
| N2···H | 0.016 | 0.053 | 0.011 | -0.009 | 0.002 | 1.207 |
| 2···C$_2$NH$_4$ | Se···N3 | 0.023 | 0.056 | 0.014 | -0.013 | 0.000 | 1.024 |
| N2···H | 0.009 | 0.032 | 0.007 | -0.005 | 0.002 | 1.322 |
| 2···m-C$_2$N$_2$H$_5$ | Se···N3 | 0.021 | 0.053 | 0.012 | -0.012 | 0.001 | 1.069 |
| N2···H | 0.009 | 0.033 | 0.007 | -0.005 | 0.002 | 1.330 |
| 2···o-C$_2$N$_2$H$_5$ | Se···N3 | 0.019 | 0.051 | 0.012 | -0.011 | 0.001 | 1.095 |
| N2···H | 0.019 | 0.067 | 0.014 | -0.012 | 0.002 | 1.194 |
| 3···NCF | Te···N3 | 0.009 | 0.029 | 0.006 | -0.005 | 0.001 | 1.285 |
| N2···C | 0.010 | 0.035 | 0.007 | -0.006 | 0.002 | 1.253 |
| 3···NCCI | Te···N3 | 0.010 | 0.031 | 0.006 | -0.005 | 0.001 | 1.251 |
| N2···C | 0.008 | 0.028 | 0.006 | -0.004 | 0.001 | 1.327 |
| 3···NP | Te···N3 | 0.012 | 0.033 | 0.007 | -0.006 | 0.001 | 1.195 |
| N2···P | 0.013 | 0.035 | 0.008 | -0.007 | 0.001 | 1.164 |
| 3···N$_2$H$_2$ | Te···N3 | 0.027 | 0.055 | 0.015 | -0.016 | -0.001 | 0.928 |
| N2···H | 0.020 | 0.063 | 0.014 | -0.012 | 0.002 | 1.143 |
| 3···C$_2$NH$_4$ | Te···N3 | 0.031 | 0.060 | 0.017 | -0.020 | -0.002 | 0.878 |
| N2···H | 0.011 | 0.038 | 0.008 | -0.006 | 0.002 | 1.288 |
| 3···m-C$_2$N$_2$H$_5$ | Te···N3 | 0.032 | 0.063 | 0.018 | -0.021 | -0.002 | 0.883 |
| N2···H | 0.010 | 0.038 | 0.008 | -0.006 | 0.002 | 1.297 |
| 3···o-C$_2$N$_2$H$_5$ | Te···N3 | 0.029 | 0.061 | 0.017 | -0.019 | -0.002 | 0.909 |
| N2···H | 0.025 | 0.080 | 0.018 | -0.017 | 0.002 | 1.091 |
values greater than 1, corresponding to a purely closed-shell noncovalent interaction.

**MFDD analyses**

According to Politzer et al. [54–56], polarization is a real physical phenomenon, corresponding to the electron density shifts from one molecule to the electric field of another. Dispersion is a part of the polarization that occurs when two species approach each other. In order to achieve a visual description of the electron density shift upon complexation, the maps of molecular formation density difference (MFDD) were calculated and plotted, as shown in Fig. 5. The red regions represent gains of electron density due to intermolecular interactions and losses are shown in blue. The lone pair outside the N atom of nitrogen base causes a decrease ($\Delta n_{e1}$) in the electric field adjacent to chalcogen atom and an increase ($\Delta n_{e2}$) of electron density in region between Ch and N atoms. Meanwhile, the lone pair outside the N atom of benzochalcogendiazole causes an increase ($\Delta n_{e3}$) of electron density in region between N atom and C/P/H atom of nitrogen base, indicating that polarization plays a role in the formation of the complexes. Table 3 lists the integral values ($\Delta n_i$) of the negative and positive charges of the density difference in the corresponding regions. For the complexes

| Complex       | $\Delta n_{e1}$ | $\Delta n_{e2}$ | $\Delta n_{e3}$ |
|---------------|-----------------|-----------------|-----------------|
| 1···NCF       | −0.022          | −               | 0.011           |
| 1···NCCl      | −0.024          | −               | 0.009           |
| 1···NP        | −0.023          | −               | 0.007           |
| 1···N$_2$H$_2$| −0.030          | 0.008           | 0.017           |
| 1···C$_2$NH$_4$| −0.048          | 0.006           | 0.011           |
| 1···$m$-$C_3$N$_2$H$_4$-a | −0.055 | 0.007 | 0.014 |
| 1···$o$-$C_3$N$_2$H$_4$-a | −0.047 | 0.008 | 0.028 |
| 2···NCF       | −0.028          | −               | 0.013           |
| 2···NCCl      | −0.030          | −               | 0.010           |
| 2···NP        | −0.033          | −               | 0.009           |
| 2···N$_2$H$_2$| −0.037          | 0.010           | 0.021           |
| 2···C$_2$NH$_4$| −0.060          | 0.008           | 0.015           |
| 2···$m$-$C_3$N$_2$H$_4$-a | −0.070 | 0.009 | 0.018 |
| 2···$o$-$C_3$N$_2$H$_4$-a | −0.063 | 0.010 | 0.034 |
| 3···NCF       | −0.038          | −               | 0.015           |
| 3···NCCl      | −0.040          | −               | 0.012           |
| 3···NP        | −0.048          | −               | 0.009           |
| 3···N$_2$H$_2$| −0.050          | 0.013           | 0.027           |
| 3···C$_2$NH$_4$| −0.074          | 0.011           | 0.019           |
| 3···$m$-$C_3$N$_2$H$_4$-a | −0.095 | 0.012 | 0.024 |
| 3···$o$-$C_3$N$_2$H$_4$-a | −0.087 | 0.013 | 0.042 |
involving sp-hybridized base, the chalcogen bond is so weak that there is no basin between Ch and N atoms. From Ch = S to Se and Te, more and more electron shift ($\Delta n_{e1}$) between the Ch···N region means increasingly strong ChB interactions. Compare $\Delta n_{e2}$ and $\Delta n_{e3}$, polarization of secondary interaction is larger than that of ChB interaction.

| Complex   | $\Delta E_{\text{ele}}$ | $\Delta E_{\text{pol}}$ | $\Delta E_{\text{disp}}$ | $\Delta E_{\text{exch}}$ | $\Delta E_{\text{rep}}$ | $\%\Delta E_{\text{ele}}$ | $\%\Delta E_{\text{pol}}$ | $\%\Delta E_{\text{disp}}$ |
|-----------|-------------------------|--------------------------|---------------------------|--------------------------|--------------------------|---------------------------|---------------------------|---------------------------|
| 1···NCF   | -18.7                   | -3.2                     | -39.9                     | 21.4                     | 27.0                     | 30%                       | 5%                        | 65%                       |
| 1···NCCI  | -15.8                   | -2.0                     | -42.6                     | 24.0                     | 24.4                     | 26%                       | 3%                        | 70%                       |
| 1···NP    | -17.8                   | -4.4                     | -38.4                     | 18.8                     | 30.5                     | 29%                       | 7%                        | 63%                       |
| 1···N$_2$H$_2$ | -35.4               | -13.1                    | -50.9                     | 21.9                     | 56.7                     | 36%                       | 13%                       | 51%                       |
| 1···C$_5$NH$_5$ | -34.8              | -13.2                    | -52.1                     | 20.8                     | 59.8                     | 35%                       | 13%                       | 52%                       |
| 1···o-C$_3$N$_2$H$_4$-a | -34.9         | -11.7                    | -50.7                     | 21.7                     | 53.8                     | 36%                       | 12%                       | 52%                       |
| 1···o-C$_3$N$_2$H$_4$-a | -47.1         | -16.8                    | -56.1                     | 23.0                     | 66.3                     | 39%                       | 14%                       | 47%                       |
| 2···NCF   | -23.6                   | -5.5                     | -45.7                     | 22.9                     | 34.2                     | 31%                       | 7%                        | 61%                       |
| 2···NCCI  | -20.4                   | -4.3                     | -48.9                     | 25.7                     | 31.3                     | 28%                       | 6%                        | 66%                       |
| 2···NP    | -25.1                   | -8.3                     | -46.6                     | 20.5                     | 42.1                     | 31%                       | 10%                       | 58%                       |
| 2···N$_2$H$_2$ | -51.4               | -26.1                    | -58.4                     | 18.5                     | 89.6                     | 38%                       | 19%                       | 43%                       |
| 2···C$_5$NH$_5$ | -60.7              | -32.1                    | -63.1                     | 13.5                     | 112.2                    | 39%                       | 21%                       | 40%                       |
| 2···o-C$_3$N$_2$H$_4$-a | -59.2         | -28.3                    | -60.9                     | 15.5                     | 100.1                    | 40%                       | 19%                       | 41%                       |
| 2···o-C$_3$N$_2$H$_4$-a | -70.5         | -33.2                    | -66.0                     | 17.5                     | 111.2                    | 42%                       | 20%                       | 39%                       |
| 3···NCF   | -32.4                   | -10.5                    | -52.9                     | 23.5                     | 47.2                     | 34%                       | 11%                       | 55%                       |
| 3···NCCI  | -29.5                   | -10.0                    | -56.6                     | 26.7                     | 45.7                     | 31%                       | 10%                       | 59%                       |
| 3···NP    | -44.4                   | -23.7                    | -59.4                     | 18.0                     | 81.8                     | 35%                       | 19%                       | 47%                       |
| 3···N$_2$H$_2$ | -86.4               | -59.4                    | -66.3                     | 3.3                      | 163.6                    | 41%                       | 28%                       | 31%                       |
| 3···C$_5$NH$_5$ | -95.0              | -63.2                    | -74.1                     | -0.8                     | 181.6                    | 41%                       | 27%                       | 32%                       |
| 3···m-C$_3$N$_2$H$_4$-a | -105.1          | -66.8                    | -71.9                     | -4.0                     | 191.6                    | 43%                       | 27%                       | 29%                       |
| 3···o-C$_3$N$_2$H$_4$-a | -117.2          | -72.6                    | -76.9                     | -1.5                     | 203.0                    | 44%                       | 27%                       | 29%                       |

Fig. 6 Molecular graphs of the representative ternary complexes
Table 5 Total binding energy (ΔE_{total}), binding energy in the ternary complexes (ΔE_{AB,T}), their change (ΔΔE_{AB}) and the increased percentage (%ΔE_{AB}) relative to the binary complexes, and the cooperative energy (E_{coop}) (energies are in kJ/mol)

| Complexes B···A···B | ΔE_{total} | ΔE_{A···B,T} | ΔΔE_{A···B} | %ΔE_{A···B} | E_{coop} | ρ_b(Ch···N3) | ρ_b(N2···C/P/H) |
|---------------------|------------|--------------|-------------|-------------|----------|--------------|---------------|
| NCF···1····NCF       | −22.9      | −10.8        | 1.3         | −11%        | 1.3      | -            | 0.009         |
| NCCI···1····NCCI     | −22.7      | −10.4        | 1.3         | −16%        | 2.0      | 0.005        | 0.007         |
| NP···1····NP         | −22.9      | −10.2        | 2.4         | −19%        | 2.4      | 0.005        | 0.009         |
| N\textsubscript{H}\textsubscript{2}···1····N\textsubscript{H}\textsubscript{2} | −32.3 | −15.9 | 0.6 | −3% | 0.6 | 0.011 | 0.014 |
| C\textsubscript{4}\textsubscript{H}\textsubscript{8}···1····C\textsubscript{4}\textsubscript{H}\textsubscript{8} | −33.8 | −16.1 | 1.6 | −9% | 1.6 | 0.013 | 0.007 |
| a-m-C\textsubscript{6}N\textsubscript{4}H\textsubscript{4}···1····m-C\textsubscript{6}N\textsubscript{4}H\textsubscript{4} | −34.3 | −15.0 | 4.3 | −22% | 4.3 | 0.012 | 0.008 |
| a-o-C\textsubscript{3}N\textsubscript{2}H\textsubscript{4}···1····o-C\textsubscript{3}N\textsubscript{2}H\textsubscript{4} | −51.4 | −24.7 | 2.0 | −8% | 2.0 | 0.012 | 0.017 |
| NCF···2····NCF       | −31.4      | −15.2        | 1.1         | −6%         | 1.1      | 0.007        | 0.009         |
| NCCI···2····NCCI     | −31.7      | −15.0        | 1.7         | −10%        | 1.7      | 0.007        | 0.007         |
| NP···2····NP         | −33.6      | −15.8        | 1.9         | −11%        | 1.9      | 0.007        | 0.009         |
| N\textsubscript{H}\textsubscript{2}···2····N\textsubscript{H}\textsubscript{2} | −47.3 | −23.2 | 0.9 | −4% | 0.9 | 0.015 | 0.018 |
| C\textsubscript{2}H\textsubscript{4}···2····C\textsubscript{2}H\textsubscript{4} | −51.1 | −22.9 | 5.5 | −19% | 5.4 | 0.018 | 0.009 |
| a-m-C\textsubscript{6}N\textsubscript{4}H\textsubscript{4}···2····m-C\textsubscript{6}N\textsubscript{4}H\textsubscript{4} | −53.5 | −23.8 | 6.0 | −20% | 6.0 | 0.017 | 0.009 |
| a-o-C\textsubscript{3}N\textsubscript{2}H\textsubscript{4}···2····o-C\textsubscript{3}N\textsubscript{2}H\textsubscript{4} | −73.1 | −35.5 | 2.2 | −6% | 2.2 | 0.017 | 0.020 |
| NCF···3····NCF       | −43.8      | −21.5        | 0.8         | −4%         | 0.8      | 0.009        | 0.010         |
| NCCI···3····NCCI     | −44.8      | −21.5        | 1.7         | −7%         | 1.7      | 0.009        | 0.008         |
| NP···3····NP         | −51.3      | −24.7        | 1.9         | −7%         | 1.9      | 0.010        | 0.013         |
| N\textsubscript{H}\textsubscript{2}···3····N\textsubscript{H}\textsubscript{2} | −70.7 | −33.1 | 4.6 | −12% | 4.6 | 0.022 | 0.021 |
| C\textsubscript{4}H\textsubscript{8}···3····C\textsubscript{4}H\textsubscript{8} | −77.3 | −32.1 | 13.1 | −29% | 13.1 | 0.024 | 0.011 |
| a-m-C\textsubscript{6}N\textsubscript{4}H\textsubscript{4}···3····m-C\textsubscript{6}N\textsubscript{4}H\textsubscript{4} | −82.3 | −33.8 | 14.8 | −30% | 14.8 | 0.023 | 0.011 |
| a-o-C\textsubscript{3}N\textsubscript{2}H\textsubscript{4}···3····o-C\textsubscript{3}N\textsubscript{2}H\textsubscript{4} | −107.2 | −50.2 | 6.8 | −12% | 6.8 | 0.023 | 0.026 |

\[ \Delta E_{total} = E_{BB} - E_A \cdot 2E_B + E_{AB} \cdot \Delta E_{(AB,T)} \]
\[ \Delta E_{A···B,T} = \Delta E_{A···B} - \Delta E_{AB} \cdot \Delta E_{(AB,D)} \]
\[ \%\Delta E_{A···B} = (\Delta E_{A···B} - \Delta E_{(AB,D)})/\Delta E_{(AB,T)} \]
\[ E_{coop} = \Delta E_{total} - (2\Delta E_{(AB,D)} + \Delta E_{(BB,D)}) \]

Energy decomposition analysis

A partitioning of the total interaction energy of each complex into its individual contributing factors can provide useful insights into its origins. In order to gain further understanding of the nature of the complexes, we performed an energy decomposition analysis within the GAMESS package. The total interaction energy is composed of five parts: electrostatic energy (ΔE_{ele}), exchange energy (ΔE_{exch}), repulsion energy (ΔE_{rep}), polarization energy (ΔE_{pol}) and dispersion energy (ΔE_{disp}), which are listed in Table 4.

From Table 4, ΔE_{exch} were determined to be positive values for most complexes except for 3···N-bases with sp\textsuperscript{2} hybrid, i.e., a repulsive energy. For the sulfur complexes, the dispersion interaction was found to play a prominent role with its contribution (%ΔE_{disp}) ranging from 47 to 70% of the total attractive force, the contribution of electrostatic force (%ΔE_{ele}) is in the range of 26−39%, and polarization contributes little. From Ch = S to Se and Te, the contribution of dispersion decreases, while that of electrostatic force and polarization increases gradually. For the weak selenium and tellurium complexes involving sp-hybridized N-bases, dispersion still plays a major role. The contribution of electrostatic is equivalent to that of dispersion for the selenium complexes involving sp\textsuperscript{2}-hybridized N-bases. The electrostatic force makes the biggest contribution, and polarization is comparable to dispersion for the tellurium complexes containing sp\textsuperscript{2}-hybridized N-bases.

Cooperativity in the 1:2 complexes

The optimized geometries of the representative 1:2 complexes are shown in Fig. 6. It can be seen that N-bases are symmetrically distributed on both sides of the benzochalagonadiazoles and have the same topological properties at the intermolecular BCPs. The energetic and topological parameters are collected in Table 5. The total binding energy (ΔE_{total}) is calculated as the energy of ternary complex minus the sum of the optimized monomers, the cooperative energy (E_{coop}) is defined as the difference of the total binding energy in the ternary complex with the sum of the binding energy in the respective binary complexes. The total binding energy varies from −22.7 kJ/mol\textsuperscript{1} in NCCI···1····NCCI to −107.2 kJ/mol in a-o-C\textsubscript{3}N\textsubscript{2}H\textsubscript{4}···3····o-C\textsubscript{3}N\textsubscript{2}H\textsubscript{4}···a. The binding energies (ΔE_{A···B,T}) between benzochalagonadiazole and N-base in the ternary complexes are less negative than those in the binary complexes, indicating that the addition of N-base weakens the intermolecular
interactions. The positive $E_{\text{coop}}$ values also illustrate the anti-cooperative effects in the 1:2 complexes. The values of decreased percentage ($\% \Delta E_{A-B}$) and $E_{\text{coop}}$ are in the range of $-3$ to approximately $-30\%$ and $0.6-14.8$ kJ/mol, which is independent of the strength of the binary complex. For example, the binding energy of $3\cdots N_2 H_4$, $3\cdots C_5 NH_5$, $3\cdots m-C_3 N_2 H_4-a$, and $3\cdots o-C_3 N_2 H_4-a$ is $-37.6$, $-45.2$, $-48.7$, and $-56.9$ kJ/mol, while that of electrostatic force and polarization increases = S to Se and Te, the contribution of dispersion decreases, $\% \Delta E_{A-B}$ value is $-12\%$, $-29\%$, $-30\%$, and $-12\%$ for $N_2 H_4\cdots 3\cdots N_2 H_4$, $C_5NH_5\cdots 3\cdots C_5NH_5$, $a$-$m$-$C_3 N_2 H_4\cdots 3\cdots m$-$C_3 N_2 H_4-a$, and $a$-$o$-$C_3 N_2 H_4\cdots 3\cdots o$-$C_3 N_2 H_4-a$, respectively. This case may be related to the relative strength of chalcogen and hydrogen bonds; the stronger chalcogen bond shows greater synergistic effect.

The cooperativity in the 1:2 complex is also estimated with the electron density at the intermolecular BCP. From Tables 5, it can be seen that the electron density ($\rho_b$) at the ChB BCP in the ternary complex is smaller than the corresponding density in the binary complex, while $\rho_b$ at the BCP of secondary interaction pretty much constant. For example, $\rho_b$ at the Te$\cdots$N3 and N2$\cdots$H BCPs is 0.032 a.u. and 0.011 a.u. in $3\cdots m$-$C_3 N_2 H_4-a$, it becomes 0.023 a.u. and 0.011 a.u. in $a$-$m$-$C_3 N_2 H_4\cdots 3\cdots m$-$C_3 N_2 H_4-a$. These results indicate that bifurcated Chb in the 1:2 complex is weaker than ChB in the binary complex, $\pi$-hole bond, pnicogen bond, or hydrogen bond is unchanged.

**Conclusion**

The Ch$\cdots$N chalcogen bonds and the secondary interactions between tetrafluoro-benzochalcogenadiazoles (chalcogen = S, Se, Te) and a series of nitrogen bases (FCN, CICN, NP, trans-$N_2 H_2$, pyridine, pyrazole, imidazole) were investigated at the B97-D3/def2-TZVP level of theory. The binding energies become more negative in the sequence Ch = S < Se < Te and N-base = FCN < CICN < NP < $N_2 H_2$ < $C_5NH_5$ < $m$-$C_3 N_2 H_4-a$ < $o$-$C_3 N_2 H_4-a$, with the values in the range of $-12.1$ to approximately $-56.9$ kJ/mol. From Ch = S to Se and Te, the contribution of dispersion decreases, while that of electrostatic force and polarization increases gradually. For the tellurium complexes with sp$^3$-hybridized N-bases, the electrostatic force makes the biggest contribution, and polarization is comparable to dispersion. Most of intermolecular bonds display the characters of closed-shell and noncovalent interactions, and Te$\cdots$N3 chalcogen bonds in the complexes involving sp$^2$-hybridized N-bases have the nature of partially covalent interactions. With the addition of nitrogen base, chalcogen bond becomes weaker, while the strength of secondary interaction is unchanged. In the complexes formed by $C_5NH_5$ and $m$-$C_3 N_2 H_4$, stronger chalcogen bond results in larger negative cooperativity in the 1:2 complexes.

**Author contribution** The manuscript was written through the contributions of all authors. ZL: data curation and writing—original draft. ZY: formal analysis and supervision. LX: methodology and visualization. ZX: conceptualization and writing—review and editing. All authors have read and approved the manuscript.

**Funding** This work was supported by the National Natural Science Foundation of China (Contract No. 21973027 of Prof. Li X) and Natural Science Foundation of Hebei Province (Contract Nos. B2020205002 of Prof. Li X, B2022205022 of Prof. Zeng Y).

**Data availability** The manuscript has full control of all primary data, and the authors agree to allow the journal to review their data if requested.

**Code availability** Not applicable.

**Declarations**

**Ethics approval** The manuscript complies to the Ethical Rules applicable for the journal.

**Consent to participate** The authors agree to participate in this investigation.

**Consent for publication** Written informed consent for publication was obtained from all participants.

**Conflict of interest** The authors declare no competing interests.

**References**

1. Müller-Dethlefs K, Hobza P (2000) Noncovalent interactions: a challenge for experiment and theory. Chem Rev 100:143–168
2. Scheiner S (2015) Noncovalent Forces. Springer, Cham, Switzerland
3. Scheiner S (2019) Forty years of progress in the study of the hydrogen bond. Struct Chem 30:1119–1128
4. Cavall G, Metrangolo P, Milani R, Pilati T, Priimagi A, Resnati G, Terraneo G (2016) The Halogen Bond. Chem Rev 116:2478–2601
5. Cavall G, Metrangolo P, Pilati T, Resnati G, Terraneo G (2014) Naming interactions from the electrophilic site. Cryst Growth Des 14:2697–2702
6. Alkorta I, Elguero J, Frontera A (2020) Not only hydrogen bonds: other noncovalent interactions. Crystals 10:180
7. Aakeroy CB, Bryce DL, Desiraju GR, Frontera A, Legon AC, Nicoter A, Rissanen K, Scheiner S, Terraneo G, Metrangolo P, Resnati G (2019) Definition of the chalcogen bond. Pure Appl Chem 91:1889–1892
8. Clark T, Hennemann M, Murray JS, Politzer P (2007) Halogen bonding: the $\sigma$-hole. J Mol Model 13:291–296
9. Murray JS, Lane P, Clark T, Politzer P (2007) $\sigma$-hole bonding: molecules containing group VI atoms. J Mol Model 13:1033–1038
10. Murray JS, Lane P, Politzer P (2008) Simultaneous $\sigma$-hole and hydrogen bonding by sulfur- and selenium-containing heterocycles. Int J Quantum Chem 108:2770–2781
11. Politzer P, Murray JS, Clark T (2013) Halogen bonding and other $\sigma$-hole interactions: a perspective. Phys Chem Chem Phys 15:11178–11189
12. Murray JS, Lane P, Clark T, Riley KE, Politzer P (2012) $\sigma$-holes, $\pi$-holes and electrostatically-driven interactions. J Mol Model 18:541–548
13. Mahmudov KT, Kopylovich MN, Guedes da Silva MFC, Pombeiro AJL (2017) Chalcogen bonding in synthesis, catalysis and design of materials. Dalton Trans 46:10121–10138

14. Benz S, López-Andarias J, Mareda J, Sakai N, Matile S (2017) Catalysis with chalcogen bonds. Angew Chem Int Ed 56:812–815

15. Scibar P, Terraneo G, Resnati G (2019) The chalcogen bond in crystalline solids: a world parallel to halogen bond. Acc Chem Res 52:1313–1324

16. Bliot N, Bonifazi D (2020) Chalcogen-bond driven molecular recognition at work. Coord Chem Rev 413:213243

17. Vogel L, Wonner P, Huber SM (2019) Chalcogen bonding: an overview. Angew Chem Int Ed 58:1880–1891

18. Wang W, Zhu H, Feng L, Yu Q, Hao J, Zhu R, Wang Y (2020) Dual chalcogen-chalcogen bonding catalysis. J Am Chem Soc 142:3117–3124

19. Cozzolino AF, Vargas-Baca I, Mansour S, Mahmoudkhan AH (2005) The nature of the supramolecular association of 1,2,5-chalcogenadiazoles. J Am Chem Soc 127:3184–3190

20. Berioni G, Pégot B, Marrot J, Goumont R (2009) Supramolecular association of 1,2,5-chalcogenadiazoles: an unexpected self-assembled disymmetric [Se…N4]4+ four-membered ring. CrystEngComm 11:986–988

21. Cozzolino AF, Whittlestone PS, Vargas-Baca I (2010) Supramolecular chromatophotism of the crystalline phases of 4 S 7 tetrafluorobenzo-2 1 3-telluradiazole. J Am Chem Soc 132:17265–17270

22. Kremer A, Ferri A, Bliot N, Wouters J, Bonifazi D (2016) Supramolecular wiring of benzo-1 3-chalcogenazoles through programmed chalcogen bonding interactions. Chem Eur J 22:5665–5675

23. Riwar LJ, Trapp N, Root K, Zenobi R, Diederich F (2018) Supramolecular Capsules: Strong versus Weak Chalcogen Bonding. Angew Chem Int Ed 57:17259–17264

24. Ams MR, Trapp N, Schwab A, Milić J, Diederich F (2019) Chalcogen bonding “2s−2s2 squares” versus competing interactions: exploring the recognition properties of sulfur. Chem Eur J 25:323–333

25. Lu Y, Li W, Yang W, Zhu Z, Xu Z, Liu H (2019) 2Ch−2n square and hexagon interactions: a combined crystallographic data analysis and computational study. Phys Chem Chem Phys 21:21568–21576

26. Kumar V, Xu Y, Bryce DL (2020) Double chalcogen bonds: crystal engineering stratagems via diffraction and multielectron clear solid-state magnetic resonance spectroscopy. Chem Eur J 26:3275–3289

27. Dhaqa A, Jeannin O, Aubert E, Espinosa E, Fourmigué M (2021) Supramolecular rectangles through directional chalcogen bonding. Chem Commun 57:4560–4563

28. Garrett GE, Gibson GL, Straus RN, Seferos DS, Taylor MS (2015) Chalcogen bonding in solution: interactions of benzotelluradiazoles with anionic and uncharged Lewis bases. J Am Chem Soc 137:4216–4213

29. Semenov NA, Gorbunov DE, Shakhova MV, Salnikov GE, Bagryanskaya IY, Korolev VV, Beckmann J, Gritsan NP, Zibarev AV (2018) Donor–acceptor complexes between 1,2,5-chalcogenadiazoles (Te, Se, S) and the pseudohalides X CN− and CN−X. J Phys Chem A 125:657–668

30. Cozzolino AF, Dimopoulos-Italiano G, Lee LM, Vargas-Baca I (2013) Chalcogen–nitrogen secondary bonding interactions in the gas phase—spectrometric detection of ionized benzo-2,1,3-telluradiazole Dimers. Eur J Inorg Chem 2013:2751–2756

31. Ho PC, Szydłowski P, Sinclair J, Elder PJW, Kübel J, Gendy C, Lee LM, Jenkins H, Britten JP, Morim DR, Vargas-Baca I (2016) Supramolecular macrocycles reversibly assembled by Te…O chalcogen bonding. Nat Commun 7:11299

32. Tsuzuki S, Sato N (2013) Origin of attraction in chalcogen–nitrogen interaction of 1,2,5-chalcogenadiazole dimers. J Phys Chem B 117:6849–6855

33. Haberhauer G, Gleiter R (2020) The nature of strong chalcogen bonds involving chalcogen-containing heterocycles. Angew Chem Int Ed 59:21236–21243

34. Vleeschouwer FD, Denayer M, Pinter B, Geerlings P, Proft FD (2018) Characterization of chalcogen bonding interactions via an in-depth conceptual quantum chemical analysis. J Comput Chem 39:557–572

35. Michalczyk M, Malik M, Zierkiewicz W, Scheiner S (2021) Experimental and theoretical studies of dimers stabilized by two chalcogen bonds in the presence of a N–N pnicogen bond. J Phys Chem A 125:657–668

36. Scheiner S (2022) Principles guiding the square bonding motif containing a pair of chalcogen bonds between chalcogenadiazoles. J Phys Chem A 126:1194–1203

37. Frisch MJ, Trucks GW, Schlegel HB, Scuseria GE, Ma R, Cheeseman JR, Scamani G, Barone V, Mennucci B, Petersson GA, Nakatsuji H, Caricato M, Li X, Hratchian HP, Izmaylov AF, Bloino JG, Sonnenberg JL, Hada M, Ehara M, Toyota K, Fukuda R, Hasegawa J, Ishida M, Nakajima T, Honda Y, Kitao O, Nakai H, Vreven T, Montgomery Jr JA, Peralta JE, Ogliaro F, Bearpark M, Heyd JJ, Brothers E, Kudin KN, Staroverov VN, Keith T, Kobayashi R, Normand J, Raghavachari K, Rendell A, Burant JC, Yngvar SS, Tomasi J, Cossi M, Rega N, Millam JM, Klene M, Knox JE, Cross JB, Bakken V, Adamo C, Jaramillo J, Gomperts R, Stratmann RE, Yazyev O, Austin AJ, Cammi R, Pomelli C, Ochterski JW, Martin RL, Morokuma K, Zakrzewski VG, Voth GA, Salvador P, Dannenberg JG, Dapprich S, Daniels AD, Farkas O, Foresman JB, Ortiz JV, Cioslowski J, Fox DJ (2013) Gaussian 09, Revision D.01, Gaussian Inc., Wallingford CT

38. Boys SF, Bernardi F (1970) The calculation of small molecular interactions by the differences of separate total energies, some procedures with reduced errors. Mol Phys 19:553–566

39. Schmidt MW, Baldridge KK, Boatz JA, Elbert ST, Gordon MS, Jensen JH, Koseki S, Matsunaga N, Nguyen KA, Su SJ, Windus TL, Dupuis M, Montgomery JA (1993) General atomic and molecular electronic structure system. J Comput Chem 14:1347–1363

40. Su PF, Li H (2009) Energy decomposition analysis of covalent bonds and intermolecular interactions. J Chem Phys 131:014102

41. Bulat FA, Toro-Labbé A, Brinic T, Murray JS, Politzer P (2010) Quantitative analysis of molecular surfaces: areas, volumes, electrostatic potentials and average local ionization energies. J Mol Model 16:1679–1691

42. Keith TA (2015) Computational improvements for the theory of atoms in molecules. AIMA (2015) 24581–3590

43. Bondi A (1964) Van der Waals volumes and radii. J Phys Chem 68:441–447

44. Humphrey W, Dalke A, Schulten K (1996) VMD: visual molecular dynamics. J Mol Graph 14:33–38

45. Nizko VDPN, Scheiner S (2016) Comparison of π-hole tetrel bonding with π-hole halogen bonds in complexes of XCN (X = F, Cl, Br, I) and NH2. Phys Chem Chem Phys 18:3581–3590

46. Bondi A (1964) Van der Waals volumes and radii. J Phys Chem 68:441–447

47. Johnson ER, Keinan S, Mori-Sanchez P, Contreras-Garcia J, Cohen AJ, Yang W (2010) Revealing noncovalent interactions. J Am Chem Soc 132:6498–6506

48. Contreras-Garcia J, Johnson ER, Keinan S, Claudert R, Pique-mal JP, Beratan DN (2011) Yang W NCIPLOT: A Program for Plotting Noncovalent Interaction Regions. J Chem Theory Comput 7:625–632

49. Bader RFW (1991) A quantum theory of molecular structure and its applications. Chem Rev 91:893–928

50. Becker A, Matta CF, Boyd RJ (2007) The quantum theory of atoms in molecules. Wiley, New York
51. Espinosa E, Molins E, Lecomte C (1998) Hydrogen bond strengths revealed by topological analyses of experimentally observed electron densities. Chem Phys Lett 285:170–173
52. Bauzá A, Fronter A (2020) Halogen and chalcogen bond energies evaluated using electron density properties. ChemPhysChem 21:26–31
53. Cremer D, Kraka E (1984) Chemical bonds without bonding electron density — does the difference electron-density analysis suffice for a description of the chemical bond? Angew Chem Int Ed 23:627–628
54. Politzer P, Riley KE, Bulat FA, Murray JS (2012) Perspectives on halogen bonding and other r-hole interactions: lex parsimony (Occam’s Razor). Comput Theor Chem 998:2–8
55. Politzer P, Murray JS, Clark T (2015) Mathematical modeling and physical reality in noncovalent interactions. J Mol Model 21:52
56. Murray JS, Politzer P (2020) Interaction and Polarization Energy Relationships in σ-Hole and π-Hole Bonding. Crystals 10:76

Publisher's note Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.

Springer Nature or its licensor holds exclusive rights to this article under a publishing agreement with the author(s) or other rightsholder(s); author self-archiving of the accepted manuscript version of this article is solely governed by the terms of such publishing agreement and applicable law.