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Can we quantitatively evaluate the mutual impacts of intramolecular metal–ligand bonds the same as intermolecular noncovalent bonds?†

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In this paper, we have reviewed several equations for calculating the cooperative energy of two chemical bonds between three fragments/species, regardless of whether they are atoms, ions or molecules, and whether the bonds between them are intra- or intermolecular. It is emphasized that two chemical bonds upon cooperation in a new compound change the bond dissociation energy of each other exactly by the same quantitative value, their cooperative energy, regardless of the nature of the bonds or whether one bond is very weak and another one is very strong. However, the final benefit/drawback of weak bonds from this cooperation can be considerably larger than that of strong bonds. The above statements are supported by a computational study on the various types of inter- and intramolecular chemical bonds.

1. Introduction

Understanding the possible effects of chemical bonds on each other and the total stability of a system of bonds will help us to design the desired molecular and supramolecular systems rationally. Among all types of chemical bonds, only the mutual impact of intermolecular noncovalent bonds on the strength of each other, named the cooperativity of bonds, has been extensively studied during the last six decades.[1] There are some well-known methodologies for the evaluation of the cooperativity of noncovalent bonds and the calculation of related cooperative energies. The following equations have been frequently used for the evaluation of the cooperativity of coinage-metal bonds with other types of interactions[2–13] and also that of intermolecular noncovalent bonds, especially those including hydrogen bonds,[14–25] dihydrogen bonds,[26–28] beryllium bonds,[29,30] lithium bonds,[31–34] lithium–π,[35] halogen bonds,[36–48] chalcogen bonds,[49–51] pnicogen bonds,[52–56] cation–π interactions,[57–60] anion–π interactions,[61–63] π···π interactions,[64] σ-hole[65,66] and π-hole[67–70] interactions in ternary systems.

$$\Delta_{\mathrm{ABC}} = \mathrm{IE}^{\mathrm{total}}_{\mathrm{ABC}} - (\mathrm{IE}^{\mathrm{ABC}}_{\mathrm{A-B}} + \mathrm{IE}^{\mathrm{ABC}}_{\mathrm{B-C}} + \mathrm{IE}^{\mathrm{ABC}}_{\mathrm{A-C}}) \quad (1)$$

$$E_{\mathrm{coop}} = \mathrm{SE}_{\mathrm{ABC}} - (\mathrm{SE}_{\mathrm{AB}} + \mathrm{SE}_{\mathrm{BC}} + \mathrm{SE}^{\mathrm{ABC}}_{\mathrm{AC}}) \quad (2)$$

$$E_{\mathrm{coop}} = \mathrm{SE}_{\mathrm{ABC}} - (\mathrm{SE}_{\mathrm{AB}} + \mathrm{SE}_{\mathrm{BC}}) \quad (3)$$

In the above equations, Δ_{ABC} and E_{coop} correspond to the three-body term[71–77] and cooperative energy, respectively. The term $\mathrm{IE}^{\mathrm{total}}_{\mathrm{ABC}}$ is used for the value of the total interaction energy of the ABC system, and the terms $\mathrm{IE}^{\mathrm{ABC}}_{\mathrm{AB}}$, $\mathrm{IE}^{\mathrm{ABC}}_{\mathrm{BC}}$ and $\mathrm{IE}^{\mathrm{ABC}}_{\mathrm{AC}}$ are used for pairwise interaction energies in the structure of the ABC system. Also, the term $\mathrm{SE}_{\mathrm{ABC}}$ is used for the total stabilization energy of a ternary system, and the terms $\mathrm{SE}_{\mathrm{AB}}$ and $\mathrm{SE}_{\mathrm{BC}}$ are used for the stabilization energy of the corresponding isolated AB and BC systems in their optimized geometries, respectively. The term $\mathrm{SE}^{\mathrm{ABC}}_{\mathrm{AC}}$ also represents the stabilization energy of the AC pair frozen into the geometry of the ABC system. To the best of our knowledge, still, two following important questions have never been clearly answered:

(I) Can we quantitatively evaluate the cooperative energies of all types of chemical bonds?

(II) Do chemical bonds have the same impacts on the values of bond dissociation energies of each other?

The main aim of this paper is to answer both the above important questions. Herein, we show that in agreement with the law of conservation of energy and Hess's law, two A–B and B–C chemical bonds upon cooperation in a new ABC compound change the energy of each other exactly by the same quantitative value, even when one bond is very strong and the other one is very weak. One can arbitrarily name such a phenomenon the "intrinsic cooperativity of bonds", and evaluate it for all types of chemical bonds using the equations recommended here. Several equations are proposed and used for calculating the total stabilization and interaction energies of ABC systems and the cooperativity of bonds in such systems. All equations are tested in different ABC systems with

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intermolecular noncovalent bonds or intramolecular metal–ligand bonds.

2. Theoretical methods

The geometries of all systems of intermolecular bonds (compounds **1** to **6**) were fully optimized at the DFT level with the BP86-D3(BJ)[78] functional (a DFT function and D3 version of Grimme's dispersion with Becke–Johnson damping for dispersion correction) and also the MP2[79–82] method in combination with aug-cc-pVTZ[83,84] and def2-TZVP[85,86] basis sets using the GAUSSIAN-09[87] program without any symmetry restrictions for all the above compounds. For compounds **1** to **6**, the data at BP86-D3(BJ)/def2-TZVP and MP2/def2-TZVP levels of theory are given in the ESI.† Similarly, the geometries of all systems of intramolecular metal–ligand bonds (compounds **7** to **12**) were fully optimized at the DFT level with the BP86-D3(BJ) functional and also MP2 method in combination with the def2-TZVP basis set. In the case of molybdenum, gold, mercury and lead metal ions, the inner shell electrons were modelled by effective core potentials (ECPs), which reduce the required basis set size and account for scalar relativistic effects.[85,86,88] In the case of compound **8**, exceptionally, the geometry of the complex was optimized at the MP2/def2-SVP level of theory. In all cases, vibrational frequency analysis, calculated at the above levels of theory, indicates that the optimized structures are at the stationary points corresponding to local minima without any imaginary frequency. Herein, we use the terms stabilization energy (SE), bond dissociation energy (BDE), and interaction energy (IE) when we refer to how much a system is energetically more stable than its isolated components, how much the required energy for dissociation of a defined bond, and how much is the attractive/repulsive energy between some species frozen into the geometry of a system, respectively (see also Fig. 1). The energy required for the probable deformation of a species upon interaction with other species is also shown as Es. Indeed, the deformation or strain energy (Es) is the difference between the values of stabilization or bond dissociation energies and interaction energies. The larger positive value of Es is a reason for a larger difference between SE (or –BDE) and IE values (see Fig. 1).[89–97] The following equations, for instance, show how we calculate the total stabilization of an ABC system ($\mathrm{SE_{ABC}}$), the bond dissociation energy of an A–BC bond ($\mathrm{BDE_{A-BC}}$) and also its interaction energy ($\mathrm{IE^{ABC}_{A-BC}}$):

$$\mathrm{SE_{ABC}} = E_{\mathrm{ABC}} - (E_{\mathrm{A}} + E_{\mathrm{B}} + E_{\mathrm{C}}) \tag{4}$$

$$-\mathrm{BDE_{A-BC}} = E_{\mathrm{ABC}} - (E_{\mathrm{A}} + E_{\mathrm{BC}}) \tag{5}$$

$$\mathrm{IE^{ABC}_{A-BC}} = E_{\mathrm{ABC}} - (E^{\mathrm{ABC}}_{\mathrm{A}} + E^{\mathrm{ABC}}_{\mathrm{BC}}) \tag{6}$$

In the above equations, the E_{ABC}, E_{BC}, E_{A}, E_{B} and E_{C} are the electronic energies of ABC, BC, A, B and C, respectively, in their optimized geometries. On the other hand, $E^{\mathrm{ABC}}_{\mathrm{A}}$ and $E^{\mathrm{ABC}}_{\mathrm{BC}}$ are the electronic energies of A and BC frozen in the optimized geometry of ABC. All calculated SE, IE and BDE values are corrected for the basis set superposition error (BSSE), which was estimated with the counterpoise (CP) method proposed by Boys and Bernardi.[98] The corrected data are given here, and uncorrected data are given in the ESI† of the paper. However, the BSSE correction can be ignored for standard chemical bonds because it can be significantly overestimated. In this work, only in the case of compound **8**, at the MP2/def2-SVP level of theory, the BSSE corrections have large values.

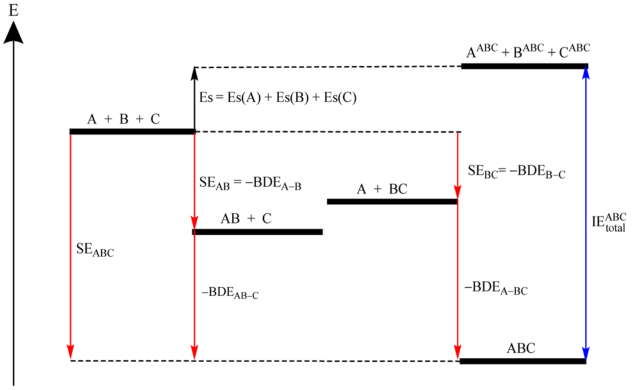


Fig. 1 Typical energy profile for the formation of AB, BC and ABC systems, along with the definition of stabilization energies (SEs) and bond dissociation energies (BDEs), as well as total deformation (strain) energy (Es) and total interaction energy ($\mathrm{IE^{ABC}_{total}}$) in the ABC system. As can be seen, it is arbitrarily assumed that the AB system is more stable than the BC system, and the bond dissociation energies (BDEs) of A–BC and AB–C bonds are larger than those of A–B and B–C bonds.

3. Results and discussion

When we want to compare the strength of two chemical bonds, we must be aware of the difference between the bond dissociation energy of a bond and its interaction energy. It is revealed that for some metastable compounds, the BDE values may even be negative.[99–101] It has been shown that when the positive value of strain (deformation) energies (Es) of species involved in the bond are larger than the negative value of their intrinsic interaction energy (IE), the BDE value (–BDE = IE + Es) will be negative.[102] Thus, in order to accurately evaluate the impact of bonds on each other, in addition to comparing the BDE values of the bonds, we have to compare their IEs. Thus, in this work, the mutual impacts of chemical bonds are studied with the comparison of both bond dissociation energies and interaction energies. Using the following equation one can show that the difference between the BDEs of the A–B and A–BC bonds, regardless of the type and nature of bonds, always is the same as that of B–C and AB–C bonds.

$$\mathrm{BDE_{A-B}} - \mathrm{BDE_{A-BC}} = \mathrm{BDE_{B-C}} - \mathrm{BDE_{AB-C}} \tag{7}$$

Let us name the left and right sides of the above equation as $\Delta\mathrm{BDE_{A-B}}$ and $\Delta\mathrm{BDE_{B-C}}$, respectively. Using eqn (8), it can be shown that the above differences in bond dissociation energies of A–B and A–BC bonds ($\Delta\mathrm{BDE_{A-B}}$) or of B–C and AB–C bonds ($\Delta\mathrm{BDE_{B-C}}$) are equal to E_{coop} calculated using eqn (3):

$$E_{\mathrm{coop}} = \Delta\mathrm{BDE_{A-B}} = \Delta\mathrm{BDE_{B-C}} \tag{8}$$

Obviously, we can correct the calculated ΔBDE_{A-B} and ΔBDE_{B-C} values, and therefore the E_{coop} values, for A···C stabilization energy (SE_{AC}).

As explained above, in this work, the mutual impact of chemical bonds is also studied with the comparison of interaction energies. However, the comparison of interaction energies of A–B and B–C bonds in AB and BC systems with those in the resulting noncyclic ABC systems usually leads to a wrong conclusion. As has been explained previously, in some cases even where the system has a negative cooperative energy (having the intrinsic positive cooperativity), the values of interaction energies for A–B and B–C bonds in the ABC system are even slightly smaller than those in the AB and BC systems, respectively.[103] Thus, in this work, in the ABC geometry, four A–B, B–C, A–BC and AB–C interaction energies are calculated and compared. Interestingly, the following useful and meaningful equation shows that, in the ABC geometry, the difference between the values of A–BC and A–B interactions is the same as that of AB–C and B–C interactions.

$$\mathrm{IE}_{\mathrm{A-BC}}^{\mathrm{ABC}} - \mathrm{IE}_{\mathrm{A-B}}^{\mathrm{ABC}} = \mathrm{IE}_{\mathrm{AB-C}}^{\mathrm{ABC}} - \mathrm{IE}_{\mathrm{B-C}}^{\mathrm{ABC}} \tag{9}$$

We name the left and right sides of the above equation as ΔIE_{A-B} and ΔIE_{B-C}, respectively. Thus, an interaction-based cooperative energy (ΔIE_{coop}) that represents the impact of two bonding interactions on the value of each other can be calculated as below:

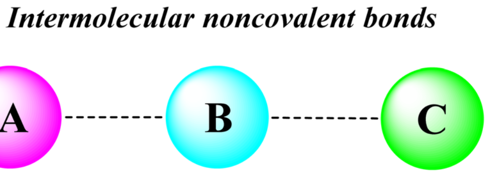
$$\Delta\mathrm{IE}_{\mathrm{coop}} = \Delta\mathrm{IE}_{\mathrm{A-B}} = \Delta\mathrm{IE}_{\mathrm{B-C}} \tag{10}$$

Once again, we can correct the calculated ΔIE_{A-B} and ΔIE_{B-C} values, and therefore the ΔIE_{coop} values, for the A···C interaction energy ($\mathrm{IE}_{\mathrm{A-C}}^{\mathrm{ABC}}$). The most important benefit of eqn (10) is that even where we have no information about AB and BC systems (for example when both or one of them is not a stable system), still in the structure of the ABC system, we can evaluate the impact of A–B and B–C interactions on each other. Obviously, with considering the data derived from both eqn (8) and (10) one can better evaluate the impact of bonds on the strength of each other.

3.1. Cooperativity in some systems of intermolecular bonds

Different types of intermolecular bonds, including the hydrogen bond, cation–π bond, chalcogen bond, halogen bond and lithium bond, were selected for the present study. The A, B and C species are defined in Fig. 2, and the optimized structures of related ABC systems are given in Fig. 3. The calculated stabilization-based and interaction-based cooperative energies are presented in Tables 1 and 2, respectively.

In all cases, the data in Table 1 confirm that the difference between the BDEs of A–B and A–BC bonds is the same as that between B–C and AB–C bonds, and can be equal to the cooperative energy of the bonds. Among the triads studied in this work, the largest percentage of changes in the value of a bond dissociation energy was observed in triad **1**, where a very weak ClF···HF (B–C) hydrogen bond upon the formation of this triad converts into the much stronger {H_3N···ClF}···HF (AB–C) hydrogen bond. The percentages of changes for the above bond are 473 and 300% at BP86-D3(BJ)/aug-cc-pVTZ and MP2/aug-cc-pVTZ levels of theory, respectively. It should be noted that HF···ClF is an alternative possible complex between the ClF and HF molecules. The HF···ClF and ClF···HF dyads upon the interaction with the NH_3 molecule form the H_3N···HF···ClF and H_3N···ClF···HF triads, respectively. While the HF···ClF dyad, having the halogen bond instead of a hydrogen bond (initially called antihydrogen bonding),[104–107] is more stable than the ClF···HF dyad, the H_3N···HF···ClF triad is less stable than the H_3N···ClF···HF triad. Indeed, the larger strength of the H_3N···ClF bond, compared to the H_3N···HF bond, and the larger cooperative energy of the bonds in the H_3N···ClF···HF triad, compared to the H_3N···HF···ClF triad, are two important reasons that H_3N···ClF···HF is the more stable triad (see Tables S1 and S2, ESI†). As can be seen in Table 1, only in the case of triad **6**, there is an intrinsic negative cooperativity (anticooperativity), where the HMgH···{Li^+···NCCl} (A–BC) and {HMgH···Li^+}···NCCl (AB–C) bonds are weaker than initial HMgH···Li^+ (A–B) and Li^+···NCCl (B–C) bonds, respectively. For a typical example, let us review the data for triad **5** (F_3CLi···NCH···HMgH). The BDEs of A–BC and AB–C bonds at the MP2/aug-cc-pVTZ level of theory are 20.91 and 6.65 kcal mol^{-1} and both of them, by a value of 2.97 kcal mol^{-1}, are larger than the corresponding values of 17.94 and 3.68 kcal mol^{-1} for BDEs of A–B and B–C bonds, respectively. Thus, according to eqn (1), the stabilization-based cooperative energy of the above bonds is −2.97 kcal mol^{-1}. Indeed, the net changes in the BDEs of the F_3CLi···NCH (A–B) and NCH···HMgH (B–C) bonds upon the formation of the F_3CLi···NCH···HMgH (ABC) triad and converting into F_3CLi···{NCH···HMgH} (A–BC) and {F_3CLi···NCH}···HMgH (AB–C) bonds, respectively, are the same. However, the related percentages of the changes are 17 and 81%, respectively. Thus, the percentage of the change, as expected, is larger for the weaker bond (NCH···HMgH). Interaction-based cooperative energies were also calculated using eqn (9) and (10). For example, for triad **5** discussed above, the values of A–B, A–BC, B–C, and AB–C interaction energies are −18.08, −21.18, −3.71, and −6.81 kcal mol^{-1}, respectively. Thus the $\mathrm{IE}_{\mathrm{A-BC}}^{\mathrm{ABC}}$ and $\mathrm{IE}_{\mathrm{AB-C}}^{\mathrm{ABC}}$ values are larger than the corresponding $\mathrm{IE}_{\mathrm{A-B}}^{\mathrm{ABC}}$ and $\mathrm{IE}_{\mathrm{B-C}}^{\mathrm{ABC}}$ values, respectively, by a value of −3.10 kcal mol^{-1}. In conclusion,



	A	B	C
1	H_3N	ClF	HF
2	F_3B	NCH	HLi
3	FH	NCH	HLi
4	H_3N	Br_2	HF
5	F_3CLi	NCH	HMgH
6	HMgH	Li^+	NCCl

Fig. 2 Species A, B and C in the triads studied in this work.

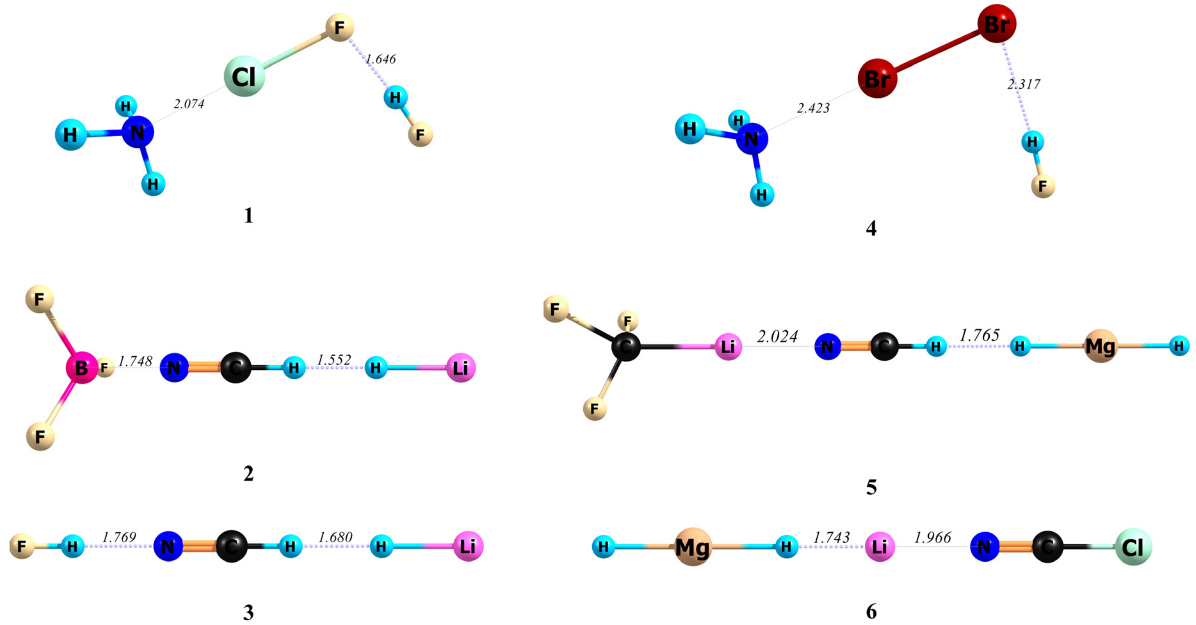


Fig. 3 The optimized structures and related A–B and B–C bond lengths (Å) of the triads studied here, at the MP2/aug-cc-pVTZ level of theory.

Table 1 Corrected[a] bond dissociation energies, cooperative energies (kcal mol^{-1}) and the percentages of changes in the bond dissociation energies of A–B and B–C bonds upon the formation of triads studied here[b]

Compound	$-BDE_{A-B}$	$-BDE_{A-BC}$	$-BDE_{B-C}$	$-BDE_{AB-C}$	SE_{ABC} [c]	E_{coop} [d]	$\%\Delta BDE_{A-B}$ [e]	$\%\Delta BDE_{B-C}$ [e]
1	−17.84	−25.65	−1.65	−9.46	−27.30	−7.81(−8.06)[f]	44%	473%
	−10.94	**−16.94**	**−2.00**	**−8.00**	**−18.94**	**−6.00(−5.70)**	**55%**	**300%**
2	−4.30	−10.14	−8.83	−14.67	−18.97	−5.84(−23.05)	136%	66%
	−5.17	**−9.18**	**−8.58**	**−12.59**	**−17.76**	**−4.01(−20.22)**	**78%**	**47%**
3	−7.69	−11.10	−8.83	−12.24	−19.93	−3.41(−2.94)	44%	39%
	−7.35	**−10.06**	**−8.58**	**−11.29**	**−18.64**	**−2.71(−1.99)**	**37%**	**32%**
4	−12.18	−15.83	−2.60	−6.25	−18.43	−3.65(−3.81)	30%	140%
	−6.81	**−9.14**	**−1.78**	**−4.11**	**−10.92**	**−2.33(−2.03)**	**34%**	**131%**
5	−17.96	−21.24	−3.85	−7.13	−25.09	−3.28(−2.46)	18%	85%
	−17.94	**−20.91**	**−3.68**	**−6.65**	**−24.59**	**−2.97(−2.09)**	**17%**	**81%**
6	−31.42	−24.56	−38.74	−31.88	−63.30	6.86(8.59)	22%	18%
	−31.17	**−25.16**	**−36.36**	**−30.35**	**−61.52**	**6.01(7.57)**	**19%**	**17%**

[a] Corrected for basis set superposition errors (BSSEs). [b] The data calculated at the BP86-D3(BJ)/aug-cc-pVTZ level of theory are given as plain text and those at the MP2/aug-cc-pVTZ level are in bold. [c] See eqn (4) and eqn (S2)–(S5) (ESI), all of which give the same value. [d] See eqn (3) and (8), both of which give the same value. [e] $\%\Delta BDE_{A-B} = \frac{|E_{coop}|}{BDE_{A-B}} \times 100, \quad \%\Delta BDE_{B-C} = \frac{|E_{coop}|}{BDE_{B-C}} \times 100.$ [f] Corrected for SE^{ABC}_{A-C}, but we do not recommend it for the above noncyclic systems (see Section 3.3).

according to eqn (10) the interaction-based cooperative energy of $F_3CLi\cdots NCH$ (A–B) and $NCH\cdots HMgH$ (B–C) bonds in the $F_3CLi\cdots NCH\cdots HMgH$ triad is −3.10 kcal mol^{-1}. The comparison of data in Tables 1 and 2 shows that in all cases, except triad **2** ($F_3B\cdots NCH\cdots HLi$), the interaction-based cooperative energies (ΔIE_{coop}) do not differ significantly from the stabilization-based cooperative energies (E_{coop}).

However, in triad **2**, the values of E_{coop} at BP86-D3(BJ)/aug-cc-pVTZ and MP2/aug-cc-pVTZ levels of theory are −5.84 and −4.01 kcal mol^{-1}, but ΔIE_{coop} values are −9.04 and −7.49 kcal mol^{-1}, respectively. Interestingly, this difference arises from the fact that the IE and BDE values only in the case of triad **2** differ significantly. The values of –BDE and IE at the MP2/aug-cc-pVTZ level of theory for the $F_3B\cdots NCH$ bond are −5.17 and −6.75 kcal mol^{-1}, respectively, and do not differ significantly (see Fig. 4a). In contrast, as shown in Fig. 4b, the values of –BDE and IE for the $F_3B\cdots\{NCH\cdots HLi\}$ bond at the same level of theory are −9.18 and −27.74 kcal mol^{-1},

Table 2 Corrected[a] calculated values for interaction energies (IE, kcal mol^{-1}) between the defined fragments frozen in the optimized geometry of the triads studied here, and related IE^{ABC}_{total}, $\%\Delta IE_{Coop}$, $\%\Delta IE_{A-B}$ and $\%\Delta IE_{B-C}$ values[b]

Compound	IE^{ABC}_{A-B}	IE^{ABC}_{A-BC}	IE^{ABC}_{B-C}	IE^{ABC}_{AB-C}	IE^{ABC}_{total} [c]	ΔIE_{coop} [d]	$\%\Delta IE_{A-B}$ [e]	$\%\Delta IE_{B-C}$ [e]
1	−24.28	−33.23	−1.94	−10.89	−35.17	−8.95(−8.23)[f]	37%	461%
	−15.24	**−23.23**	**−1.77**	**−9.76**	**−25.00**	**−7.99(−7.18)**	**52%**	**451%**
2	−20.83	−29.87	−9.95	−18.99	−39.82	−9.04(−7.70)	43%	91%
	−20.25	**−27.74**	**−8.58**	**−16.07**	**−36.32**	**−7.49(−6.05)**	**37%**	**87%**
3	−8.05	−11.78	−9.52	−13.25	−21.30	−3.73(−2.78)	46%	39%
	−7.48	**−10.46**	**−8.76**	**−11.74**	**−19.22**	**−2.98(−2.02)**	**40%**	**34%**
4	−14.34	−18.43	−2.61	−6.70	−21.04	−4.09(−3.68)	29%	157%
	−7.47	**−10.69**	**−1.55**	**−4.77**	**−12.24**	**−3.22(−2.74)**	**43%**	**208%**
5	−18.11	−21.73	−3.89	−7.51	−25.62	−3.62(−2.64)	20%	93%
	−18.08	**−21.18**	**−3.71**	**−6.81**	**−24.89**	**−3.10(−2.09)**	**17%**	**84%**
6	−31.64	−24.94	−38.93	−32.23	−63.87	6.70(7.85)	21%	17%
	−31.44	**−25.56**	**−36.52**	**−30.64**	**−62.08**	**5.88(6.89)**	**19%**	**16%**

[a] Corrected for basis set superposition errors (BSSEs). [b] The data calculated at the BP86-D3(BJ)/aug-cc-pVTZ level of theory are given as plain text and those at the MP2/aug-cc-pVTZ level are in bold. [c] See eqn (S8)–(S11) (ESI), all of which give the same value. [d] See eqn (10). [e] $\%\Delta IE_{A-B} = \frac{|\Delta IE_{coop}|}{IE^{ABC}_{A-B}} \times 100$, $\%\Delta IE_{B-C} = \frac{|\Delta IE_{coop}|}{IE^{ABC}_{B-C}} \times 100$. [f] Corrected for IE^{ABC}_{A-C}, but we do not recommend it for the above noncyclic systems (see Section 3.3).

respectively, and there is a large difference between them. We note that the planar structure of the BF_3 molecule, upon the interaction with the NCH molecule, only in the case of triad **2** changes significantly. Thus, the deformation energy of the BF_3 molecule in triad **2** is considerably larger than that in the related $F_3B\cdots NCH$ dyad. In fact, from the total deformation energies (18.56 kcal mol^{-1}) of interacted species in triad **2**, an amount of 17.66 kcal mol^{-1} belongs to the BF_3 molecule. Obviously, the calculated interaction energies do not depend only on the strength of interactions, and they increase with increasing the amount of deformation energies. In conclusion, as can be seen in Fig. 4a and b, both the IE^{ABC}_{A-B} and IE^{ABC}_{A-BC} interaction energies have a large value, and the difference between them is also relatively large. Therefore, the difference between IEs of $F_3B\cdots NCH$ (A–B) and $F_3B\cdots\{NCH\cdots HLi\}$ (A–BC) bonds ($\Delta IE_{coop} = -7.49$ kcal mol^{-1}) is considerably larger than that between BDEs of these bonds ($E_{coop} = -4.01$ kcal mol^{-1}).

On the other hand, the comparison of the values of $\%\Delta BDE_{A-B}$ and $\%\Delta IE_{A-B}$ in Tables 1 and 2, respectively, show that the percentage of change in the BDE of the $F_3B\cdots NCH$ bond (78%) is larger than that of its IE (37%). Furthermore, the data show that the $F_3B\cdots\{NCH\cdots HLi\}$ bond with a length of 1.748 Å, is considerably shorter than the $F_3B\cdots NCH$ bond, having a length of 2.361 Å (see Fig. 3 and Fig. S1, and also Table S3, ESI†). Thus, we can conclude that only the ΔIE_{coop} and $\%\Delta BDE_{A-B}$ values clearly explain why the change in the length of the $F_3B\cdots NCH$ bond is very large. In conclusion, the data for triad **2** clearly show that where the deformation energies of interacted species are very large, the comparison of the ΔIE_{coop} values and/or the percentage of change in the BDE values ($\%\Delta BDE_{A-B}$) are more reliable than the comparison of E_{coop} values. On the other hand, one may be interested in comparing the A–B and B–C interaction energies in AB and BC systems with A–BC and AB–C interaction energies in the ABC system, respectively. However, nobody has proved that the related differences are the same (*i.e.* $IE^{ABC}_{A-BC} - IE_{A-B} \neq IE^{ABC}_{AB-C} - IE_{B-C}$).

Furthermore, such comparisons sometimes will lead us to wrong conclusions. For example, in the case of triad **2**, the values of IE^{ABC}_{A-BC} and IE^{ABC}_{AB-C} at the MP2/aug-cc-pVTZ level of theory are −27.74 and −16.07 kcal mol^{-1}, while those of IE_{A-B} and IE_{B-C} for corresponding $F_3B\cdots NCH$ and $NCH\cdots HLi$ dyads are −6.75 and −8.76 kcal mol^{-1}, respectively. Thus, the difference between IE^{ABC}_{A-BC} and IE_{A-B} is −20.99 kcal mol^{-1}, while that between IE^{ABC}_{AB-C} and IE_{B-C} is −7.31 kcal mol^{-1}. Therefore, the above differences differ significantly, and in contrast to the concept of cooperativity of bonds are not the same. However, when we compare the IE^{ABC}_{A-BC} and IE^{ABC}_{A-B} values in the $F_3B\cdots NCH\cdots HLi$ triad, because the large deformation energy of the BF_3 molecule has the same effect on their values, the difference between them is not too large and is the same as that between the IE^{ABC}_{AB-C} and IE^{ABC}_{B-C} values ($\Delta IE_{coop} = -7.49$ kcal mol^{-1}).

3.2. Cooperativity in some systems of intramolecular bonds

Herein, we report the quantitative evaluation of some intramolecular metal–ligand bonds. The various types of metal complexes are selected and considered as an ABC system having two A–B and B–C bonds. The A, B and C fragments are defined in Fig. 5 and the optimized structure of complexes is presented in Fig. 6. The optimized structures of the complexes are all very similar to their available solid-state molecular structures[108–111] determined by X-ray crystallography (see also Table S12, ESI†). The data for calculating the stabilization-based and interaction-based cooperative energies are presented in Tables 3 and 4, respectively.

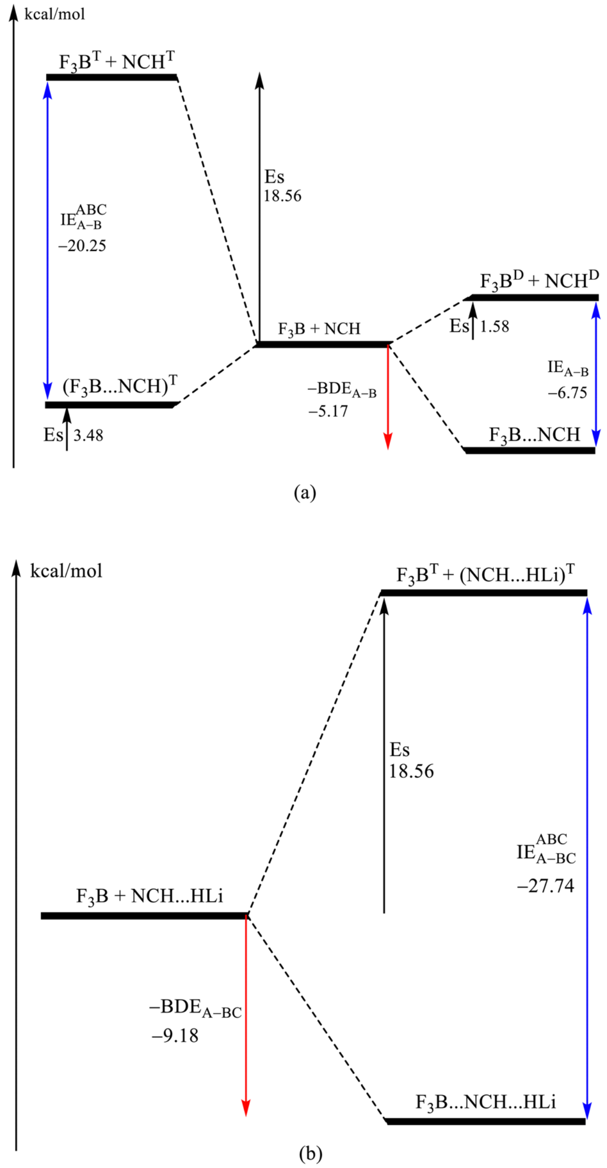
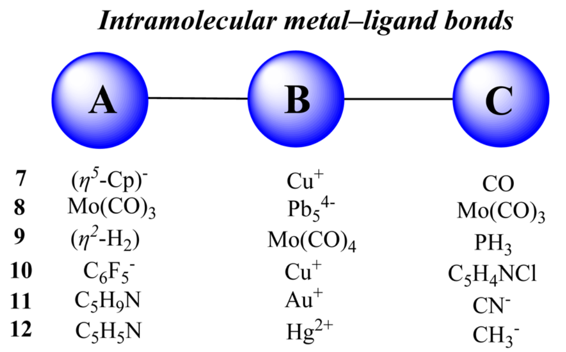


Fig. 4 Comparison of the BDEs and IEs of the A–B bond in the optimized geometry of the $F_3B\cdots NCH$ (AB) dyad and also the IE of the A–B bond in the $F_3B\cdots NCH$ (AB) dyad frozen into the optimized geometry of the $F_3B\cdots NCH\cdots HLi$ (ABC) triad (a), and comparison of the BDEs and IEs of the A–BC bond in the optimized geometry of the $F_3B\cdots NCH\cdots HLi$ triad (b).



	A	B	C
7	$(\eta^5\text{-Cp})^-$	Cu^+	CO
8	$Mo(CO)_3$	$Pb_5{}^{4-}$	$Mo(CO)_3$
9	$(\eta^2\text{-}H_2)$	$Mo(CO)_4$	PH_3
10	$C_6F_5{}^-$	Cu^+	C_5H_4NCl
11	C_5H_9N	Au^+	CN^-
12	C_5H_5N	Hg^{2+}	$CH_3{}^-$

Fig. 5 Fragments A, B and C in the metal complexes studied here.

The data show that in complex **7** there is an intrinsic positive cooperativity, while in complexes **9** to **12** an intrinsic negative cooperativity (anticooperativity) exists. For complex **7**, the calculated E_{coop} values at BP86-D3(BJ)/def2-TZVP and MP2/def2-TZVP levels of theory are −9.23 and −17.93 kcal mol^{-1}, respectively. Thus, the BDEs of $(\eta^5\text{-Cp})$–AuCO and $(\eta^5\text{-Cp})$Au–CO bonds are larger than the initial $(\eta^5\text{-Cp})$–Au and Au–CO bonds, respectively. On the other hand, the percentages of changes in the value of initial bonds at the BP86-D3(BJ)/def2-TZVP and MP2/def2-TZVP levels of theory are 5 and 10% for the $(\eta^5\text{-Cp})$–Au bond, and 19 and 55% of the Au–CO bond, respectively. Thus, while the BDEs of both the initial bonds, upon the formation of the $[(\eta^5\text{-Cp})AuCO]$ complex, change by the same quantitative value, the percentage of change for the weaker Au–CO bond is larger than that for the stronger $(\eta^5\text{-Cp})$–Au bond. Among the complexes studied here, the largest change in the bond dissociation energies occurs in the formation of the $[(C_5H_5N)Hg(CH_3)]^+$ complex, where the value of E_{coop} is +135.92 kcal mol^{-1} at the BP86-D3(BJ)/def2-TZVP level of theory, which is a good indication of the strong anticooperativity of bonds. Indeed, the BDEs of the new bonds C_5H_5N–$Hg(CH_3)$ and $(C_5H_5N)Hg$–CH_3 are smaller than the initial C_5H_5N–Hg and Hg–CH_3 bonds by a value of 135.92 kcal mol. However, the percentages of changes are different and at the above level of theory are about 68 and 26% for the C_5H_5N–Hg and Hg–CH_3 bonds, upon converting into new C_5H_5N–$Hg(CH_3)$ and $(C_5H_5N)Hg$–CH_3 bonds, respectively. We note that in the case of compound **8**, $[Pb_5\{Mo(CO)_3\}_2]^{4-}$, the BDEs of A–B, B–C, A–BC and AB–C bonds have not been calculated, as the $[Pb_5Mo(CO)_3]^{4-}$ system (AB or BC) is not a stable anion and does not exist. Indeed, it has been previously shown that the isolated $[Pb_5]^{4-}$ anion has a square pyramidal geometry, but into the geometry of the $[Pb_5\{Mo(CO)_3\}_2]^{4-}$ anion, due to the strong interactions with two $M(CO)_3$ fragments, it can be deformed into a five-membered ring with a planar geometry.[112] Therefore, in the case of the $[Pb_5\{Mo(CO)_3\}_2]^{4-}$ anion, one cannot evaluate the stabilization-based cooperative energies of bonds. However, we can quantitatively evaluate the interaction-based cooperative energies of bonds using eqn (10) and by calculating the interaction energies in the geometry of the above anion complex. As can be seen in Table 4, the value of ΔIE_{coop} for the above complex is −54.07 kcal mol^{-1}, which is a good indication of the intrinsic positive cooperativity of bonds between the $[Pb_5]^{4-}$ anion and two $M(CO)_3$ fragments. As can be seen, in all cases the differences between the IE^{ABC}_{A-B} and IE^{ABC}_{A-BC} values are the same as those between the IE^{ABC}_{B-C} and IE^{ABC}_{AB-C} ones. On the other hand, the values of interaction-based cooperative energies (ΔIE_{coop}) do not differ significantly from those of stabilization-based cooperative energies (E_{coop}). For the present complexes, similar to the triads **1** to **6** (except triad **2**), there is an excellent correlation between the calculated ΔIE_{coop} and E_{coop} values (see Fig. S5 and S6, ESI†), indicating that both

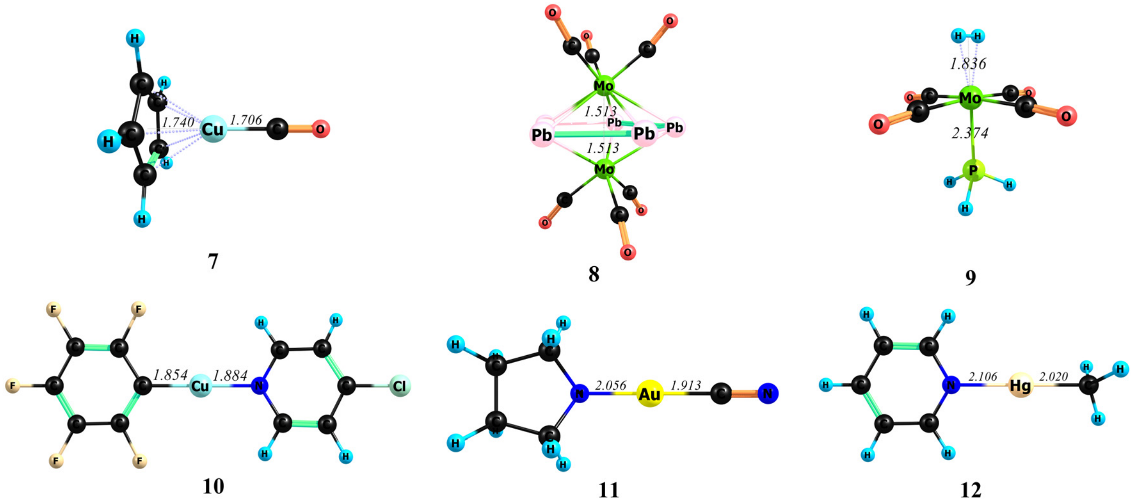


Fig. 6 The optimized structures and related A–B and B–C bond lengths (Å) for the metal complexes studied here, at the MP2/def2-TZVP level of theory for compounds **7**, **9–12**, and at the MP2/def2-SVP level in the case of compound **8**.

Table 3 Corrected[a] bond dissociation energies, cooperative energies (kcal mol^{-1}) and the percentages of changes in the bond dissociation energies of A–B and B–C bonds upon the formation of metal complexes studied here[b]

Compound	$-\mathrm{BDE}_{\mathrm{A-B}}$	$-\mathrm{BDE}_{\mathrm{A-BC}}$	$-\mathrm{BDE}_{\mathrm{B-C}}$	$-\mathrm{BDE}_{\mathrm{AB-C}}$	$\mathrm{SE}_{\mathrm{ABC}}$[c]	E_{coop}[d]	$\%\Delta\mathrm{BDE}_{\mathrm{A-B}}$[e]	$\%\Delta\mathrm{BDE}_{\mathrm{B-C}}$[e]
7	−198.26	−207.49	−47.50	−56.73	−249.99	−9.23(−7.03)[f]	5%	19%
	−184.81	**−202.74**	**−32.70**	**−50.63**	**−235.44**	**−17.93(−17.92)**	**10%**	**55%**
8[g]	—	—	—	—	−303.77	—	—	—
	—	—	—	—	**−352.21**	—	—	—
9	−34.99	−19.91	−57.64	−42.56	−77.55	15.08(11.61)	43%	26%
	−34.03	**−21.98**	**−60.98**	**−48.93**	**−82.96**	**12.05(8.84)**	**35%**	**20%**
10	−198.57	−167.15	−74.98	−43.56	−242.13	31.42(24.71)	16%	42%
	−178.54	**−162.86**	**−57.32**	**−41.64**	**−220.18**	**15.68(9.29)**	**9%**	**27%**
11	−94.23	−51.76	−227.78	−185.31	−279.54	42.47(35.47)	45%	19%
	−81.30	**−55.76**	**−214.63**	**−189.09**	**−270.39**	**25.54(17.71)**	**31%**	**12%**
12	−198.50	−62.58	−518.47	−382.55	−581.05	135.92(134.38)	68%	26%
	−172.87	**−60.78**	**−507.09**	**−395.00**	**−567.87**	**112.09(101.30)**	**65%**	**22%**

[a] Corrected for basis set superposition errors (BSSEs). [b] The data calculated at the BP86-D3(BJ)/aug-cc-pVTZ level of theory are given as plain text and those at the MP2/aug-cc-pVTZ level are in bold. [c] See eqn (4) and eqn (S2)–(S5) (ESI), all of which give the same value. [d] See eqn (3) and (8) both of which give the same value. [e] $\%\Delta\mathrm{BDE}_{\mathrm{A-B}} = \frac{|E_{\mathrm{coop}}|}{\mathrm{BDE}_{\mathrm{A-B}}} \times 100$, $\%\Delta\mathrm{BDE}_{\mathrm{B-C}} = \frac{|E_{\mathrm{coop}}|}{\mathrm{BDE}_{\mathrm{B-C}}} \times 100$. [f] Corrected for $\mathrm{SE}_{\mathrm{A-C}}^{\mathrm{ABC}}$, but we do not recommend it for the above noncyclic systems (see Section 3.3). [g] MP2 calculations for this compound were performed using the def2-SVP basis set.

the E_{coop} and $\Delta\mathrm{IE}_{\mathrm{coop}}$ values are good evidence for the comparison of the degree of the cooperativity of bonds in a series of metal complexes.

3.3. The effect of A···C interaction on cooperative energies

We remember that in a cyclic ABC system the A···C interaction cannot be ignored and one cannot use eqn (3) and (8) for calculating the synergetic effects of the bonds. However, in this work, the cooperative energies for the present noncyclic systems have been calculated and compared with and without considering the A···C interaction (see Tables 1–4). Fortunately, as the data in Tables 1–4 show, the correction of cooperative energies for $\mathrm{SE}_{\mathrm{AC}}^{\mathrm{ABC}}$ or $\mathrm{IE}_{\mathrm{AC}}^{\mathrm{ABC}}$ (see Tables S17 and S18 for their calculated values, ESI†) in all cases do not change the type of the cooperativities/anticooperativities and in most cases do not change significantly the value of cooperative energies. Herein, we prefer ignoring the A···C interaction in the noncyclic ABC systems and naming the difference between the BDEs of A–B and A–BC bonds (or B–C and AB–C bonds) as the cooperative energy of the bonds in the ABC system. In this type of nomenclature, we assume that in a noncyclic ABC system, the whole impact of A on the B–C bond and C on the A–B bond can be named the cooperative energy of A–B and B–C bonds, apart from the fact that whether A or C only change the nature of B to AB or BC, respectively, or they have also a possible interaction with each other. However, a literature review shows that most authors have not ignored the A···C interaction

Table 4 Corrected[a] calculated values for interaction energies (IE, kcal mol^{-1}) between the defined fragments frozen in the optimized geometry of metal complexes studied here, and related $\mathrm{IE}^{\mathrm{ABC}}_{\mathrm{total}}$, $\Delta\mathrm{IE}_{\mathrm{coop}}$, $\%\Delta\mathrm{IE}_{\mathrm{A-B}}$ and $\%\Delta\mathrm{IE}_{\mathrm{B-C}}$ values[b]

Compound	$\mathrm{IE}^{\mathrm{ABC}}_{\mathrm{A-B}}$	$\mathrm{IE}^{\mathrm{ABC}}_{\mathrm{A-BC}}$	$\mathrm{IE}^{\mathrm{ABC}}_{\mathrm{B-C}}$	$\mathrm{IE}^{\mathrm{ABC}}_{\mathrm{AB-C}}$	$\mathrm{IE}^{\mathrm{ABC}}_{\mathrm{total}}$[c]	$\Delta\mathrm{IE}_{\mathrm{coop}}$[d]	$\%\Delta\mathrm{IE}_{\mathrm{A-B}}$[e]	$\%\Delta\mathrm{IE}_{\mathrm{B-C}}$[e]
7	−198.37	−209.81	−45.88	−57.32	−255.69	−11.44(−8.54)[f]	6%	25%
	−184.72	**−203.15**	**−32.98**	**−51.41**	**−236.13**	**−18.43(−17.73)**	**10%**	**56%**
8[g]	−136.15	−190.22	−152.13	−206.20	−342.35	−54.07(−59.71)	40%	35%
	−184.14	**−218.13**	**−187.00**	**−220.99**	**−405.13**	**−33.99(−39.94)**	**18%**	**18%**
9	−35.61	−23.46	−57.57	−45.42	−81.03	12.15(12.02)	34%	21%
	−34.24	**−25.35**	**−61.24**	**−52.35**	**−86.59**	**8.89(8.77)**	**26%**	**14%**
10	−200.84	−169.89	−75.17	−44.22	−245.06	30.95(27.17)	15%	41%
	−180.27	**−164.82**	**−57.50**	**−42.05**	**−222.32**	**15.45(11.20)**	**9%**	**27%**
11	−93.87	−52.80	−227.76	−186.69	−280.56	41.07(35.09)	44%	18%
	−81.45	**−56.59**	**−214.77**	**−189.91**	**−271.36**	**24.86(18.00)**	**30%**	**12%**
12	−197.13	−64.40	−519.04	−386.31	−583.44	132.73(133.57)	67%	26%
	−171.42	**−63.86**	**−505.94**	**−398.38**	**−569.80**	**107.56(98.70)**	**63%**	**21%**

[a] Corrected for basis set superposition errors (BSSEs). [b] The data calculated at the BP86-D3(BJ)/aug-cc-pVTZ level of theory are given as plain text and those at the MP2/aug-cc-pVTZ level are in bold. [c] See eqn (S8)–(S11) (ESI), all of which give the same value. [d] See eqn (10). [e] $\%\Delta\mathrm{IE}_{\mathrm{A-B}} = \frac{|\Delta\mathrm{IE}_{\mathrm{coop}}|}{\mathrm{IE}^{\mathrm{ABC}}_{\mathrm{A-B}}} \times 100$, $\%\Delta\mathrm{IE}_{\mathrm{B-C}} = \frac{|\Delta\mathrm{IE}_{\mathrm{coop}}|}{\mathrm{IE}^{\mathrm{ABC}}_{\mathrm{B-C}}} \times 100$. [f] Corrected for $\mathrm{IE}^{\mathrm{ABC}}_{\mathrm{A-C}}$, but we do not recommend it for the above noncyclic systems (see Section 3.3). [g] The MP2 calculations for this compound were performed using the def2-SVP basis set.

and used eqn (1) and/or (2) for calculating the cooperative energy in noncyclic ABC systems.

On the other hand, many authors have ignored the A···C interaction and used only eqn (3) (for example see ref. 22, 23, 30–32, 35, 40, 43, 45, 49, 55, 69 and 103). Also, some other authors have used both eqn (1) and (3) at the same time (for example see ref. 14, 16, 17, 21, 36–38, 44 and 65). We note that when species A and C have a very weak interaction but their deformation energies due to a strong interaction with B are very large, the calculated value of $\mathrm{SE}^{\mathrm{ABC}}_{\mathrm{AC}}$ may have a large positive value. Thus, under such conditions, eqn (2) will give us the misleading values for the cooperative energy of the A–B and B–C bonds. Triad 2 is a good example of the above situation and the fact that previously known eqn (2) in some cases can give us misleading data. Surprisingly, due to the large Es of the BF_3 molecule in the triad **2** (see Table S19 and its footnote, ESI†), the value of the term $\mathrm{SE}^{\mathrm{AB}}_{\mathrm{AC}}$ at the MP2/aug-cc-pVTZ level of theory is +16.22 kcal mol^{-1}. Thus, as can be seen in Table 1, eqn (2) will give a value of −20.22 kcal mol^{-1} (more than 80 kJ mol^{-1}) for the E_{coop} value of triad 2 which is surprisingly larger than the total stabilization energy ($\mathrm{SE}_{\mathrm{ABC}}$) of this molecule (−17.76 kcal mol^{-1}) and also much larger than both initial bond dissociation energies (−5.17 and −8.58 kcal mol for $F_3B\cdots NCH$ and $NCH\cdots HLi$ bonds, respectively). Obviously, the above result is not logical and clearly proves that the previously known eqn (2) gives the misleading data for the cooperative energy of the $F_3B\cdots NCH$ and $NCH\cdots HLi$ bonds in triad **2**. On the other hand, eqn (3) and (8) give a value of −4.01 kcal mol^{-1} for the E_{coop} value of the above bonds in triad **2**, which is quite logical for a triad with a total stabilization energy of −17.76 kcal mol^{-1}. We note that the relatively small value of −4.01 kcal mol^{-1} (−16.78 kJ mol^{-1}) still is much larger than most of the cooperative energies found in the literature.

4. Conclusions

In this work, it is emphasized that the quantitative evaluation of the impact of chemical bonds on the strength of each other is not restricted to the intermolecular noncovalent bonds. The data showed that in agreement with the law of conservation of energy and also Hess's law the difference between the BDEs of the A–B bond in the AB system and the A–BC bond in the ABC one, is identical to that of B–C and AB–C bonds in BC and ABC systems, respectively. Interestingly, the above energy difference is identical to the energy known in the literature as cooperative energy (E_{coop}) in noncyclic ABC systems. Thus, it is shown that the intrinsic cooperativity of two chemical bonds changes their bond dissociation energies by the same value. The data also showed that in all ABC systems studied in this work, the difference between the energies of A–B and A–BC interactions is identical to that of B–C and AB–C interactions. Thus, we can similarly name the above difference as an interaction-based cooperative energy ($\Delta\mathrm{IE}_{\mathrm{coop}}$). The above quantitative value is very useful for evaluating the degree of the cooperativity of bonds in an ABC system when we have no information about the corresponding free AB and BC systems. The negative and positive values of $\Delta\mathrm{IE}_{\mathrm{coop}}$ indicate how much the attractive interaction energies are increased or decreased upon the intrinsic positive cooperativity and intrinsic negative cooperativity of bonds, respectively. The above statements were supported by a computational study on the various types of chemical bonds. Indeed, the quantitative evaluation of cooperative energies of two intramolecular bonds, similar to some systems of intermolecular noncovalent bonds, has been reported. The results showed that while, interestingly, the net changes in the bond dissociation energies of A–B and B–C bonds upon formation of an ABC system and converting into

A–BC and AB–C bonds, respectively, are the same, the percentages of the above changes are different and, as expected, are larger for weaker bonds. Fortunately, an excellent correlation was observed between the values of E_{coop} and $\Delta\text{IE}_{\text{coop}}$ for both systems of inter- and intramolecular bonds, where the deformation energies of interacted species were low. The data also showed that ignoring the A···C interaction in noncyclic systems does not change the result of our evaluation of the type of cooperativity in most cases.

Author contributions

Samaneh Sanei Movafagh: investigation, data curation, validation, and writing – original draft. Sadegh Salehzadeh: supervision, conceptualization, methodology, validation, and writing – review & editing.

Conflicts of interest

There are no conflicts of interest to declare.

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