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REGULAR ARTICLE

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An ab initio quantum chemical comparative study of possible additive rules and linear relations in parent and extended sulfur diimide families

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Abstract In this study, it has been demonstrated that there are additive rules corresponding to ab initio derived total electronic energies between members of triple sets of some extended sulfur diimides and their mono- and bi-derivatives. It has been shown that the additive rules are insensitive to the combination of methods and basis sets used to derive the total electronic energies. This insensitivity to the level of calculation is demonstrated to be the case for some linear alkanes also. It has been found that the total electronic energies of certain members of extended sulfur diimide sets ($(ZZ)_k$ and $(EE)_k$ conformers) follow a linear relation although chemical accuracy may be achieved only by excluding the smallest members of these sets. The details of this deviation have been employed to quantify the “Z-effect” proposed previously by the same authors.

Keywords Sulfur diimides · Additive rules · Linear relations · Ab initio · Density functional theory

1 Introduction

After a long-term ignorance of the community of theoretical chemists, there is a renewed interest in transferability problem and its possible consequences. Whereas transferability and related concepts have a firm ground in the history of chemistry and appeared soon in empirical theories of the nineteen century [1], less attention has been paid to their physical origins and quantitative aspects during the evolution of quantum chemistry. Thanks to Quantum Theory of Atoms in Molecules (hereafter abbreviated as QTAIM) [2], this situation has been changed and a formal definition of molecular fragments within the context of “quantum mechanics of open subsystems” [3] is now routine. Accordingly, based on such a firm theoretical ground, the putative concept of functional group and its quantitative aspects, as the cornerstones of organic chemistry, now seem to have a well-defined physics [4]. So, transferability of molecular fragments may be calculated and measured unambiguously employing QTAIM [5].

On the other hand, there were always empirical evidences regarding the possibility to transfer certain properties of molecular fragments or functional groups in a class of related molecules (particularly the homologous series). As a famous example, this quantitative transferability is best manifested in measured thermodynamic [6–8] and magnetic [9,10] properties of alkanes. In this case, methylene group ($–CH_2–$) acts as a transferable moiety. The mathematical consequences of this transferability are the additive rules and linear relations among the physical properties of a selected class of related molecules (alkanes in this case). In recent years, theoretical calculations have also been employed to demonstrate these additive rules and linear relations.

In this regard, one may note the interesting paper by Bader and Martin [11] that demonstrates the additive rule among total electronic energies (calculated by an ab initio method) of various substituted ethyl derivatives. In the three-member sets ($H–CH_2–CH_2–H$, $H–CH_2–CH_2–R$, $R–CH_2–CH_2–R$) with ($R=CH_3$, NH_2, OH, F) one may find a surprising additive rule, namely, the arithmetic mean of total electronic energies of ethane and its bi-substituted derivative is equal within chemical accuracy ($\sim$ 1–2 kcal mol^{-1}) to the total electronic energy calculated independently (at the same computational level) for its mono-substituted derivative. On the other hand, the extensive quantum chemical study of Neugebauer and Häfelinger [12] demonstrates the prevalence of linear relations in numerous organic homologous series. In every homologous series studied by these researchers, an excellent (within chemical accuracy, namely, $\sim$ 1–2 kcal mol^{-1}) linear regression has been found among total calculated electronic energies of molecules of that series and the number of corresponding electrons. In a comment on Neugebauer and Häfelinger’s paper, Cortès-Guzmán and Bader [13] demonstrate elegantly that linear relations found by the above-mentioned researchers may be explained within QTAIM definition of functional group and compensatory

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nature of energy exchange between molecular fragments (for a detailed discussion on difference between "perfect" and "compensatory" transferability see both [11,13]). So, it is safe to claim that within the context of QTAIM, additive and linear relations are both indicators of transferable fragments in many hydrocarbons and their derivatives (although as mentioned above, the "compensatory" transferability has a decisive role).

Accordingly, in this paper we have pursued the same line of attack namely, checking the presence of additive and linear relations between the total electronic energies calculated with different ab initio methods for various members of extended sulfur diimide family. As will be discussed in subsequent sections, indeed we have found regularities like those reported in alkanes and other organic homologous series. So, this paper must be viewed as a natural (and probably the first) extension of the above-mentioned research studies to "non -carbon" -containing molecules.

2 Computational details

The ab initio electronic structure calculations have been accomplished employing the standard HF and post-HF (MP2) and some DFT methods as implemented in Gaussian suite of programs [14] (for details of DFT methods and relevant references see Gaussian's internal help). Two Pople-type basis sets, namely, 6-31G(d) and 6-311+G(d,p) and also two members of correlation-consistent basis sets (cc-pVDZ and cc-pVTZ) [15,16], have been employed throughout the study. All molecules have been optimized employing tight criteria unless otherwise stated (for details of optimization procedure see Gaussian's internal help). Harmonic frequencies have been computed to discern the nature of optimized geometries (not all structures are true local minima) with the exception of HNSH–$(SN_2)_{14}$–NSNH conformers (for these structures the calculation of second derivatives of energy are out of range of our computational power). The saddle points of potential energy surfaces (PESs) have been identified according to the number of their imaginary frequencies and all have been noted in corresponding tables. In most cases, the imaginary frequencies correspond to the slightly out of plane deformations with minor energetic consequences (some of these conformers were optimized to locate corresponding non-planar local minima to verify energetic effects). Only singlet spin states have been considered in this study. Our general recipes, regarding the numerical precision of computations, have also been pursued in this study. Details may be found in a previous publication [17].

3 Some theoretical background of sulfur diimides conformational structures and clarifying various aspects of applied terminology

In the case of substituted hydrocarbons studied in this paper, the most stable conformers have always been denoted in corresponding footnotes of the relevant tables. The anti and staggered terms have been employed throughout as usually used to distinguish the celebrated Newman forms. To avoid any ambiguity, for the (OH) substituted hydrocarbons the ⟨H–O–C–C angle has also been offered in parentheses to clarify the position of hydrogen atom in hydroxyl derivative.

The main selected molecules in this study belong to sulfur diimide families (R^1–N = S = N–R^2). This family and related analogs have been the target of some theoretical investigations [17–22]. (The other relevant theoretical investigations as well as a recent bibliography on different aspects of their chemistry may be found in above-cited references.) As, they have been used only as "model" compounds for the particular propose of this study, the relevant aspects of their conformational structures alone will be discussed in this report.

Figure 1 depicts four planar conformers of the parent sulfur diimide (PSD) and their possible derivatives (structures **1**, **2**, **3** and **4**). As is evident from this figure, all the conformers may be inter-converted geometrically by changing the two dihedral angles (⟨HNSN and ⟨XNSN). Applying the same nomenclature employed in previous studies [17–22], the symbol Z has been used to denote the "0 °" dihedral angles whereas the symbol E has been employed to denote the "180 °" dihedral angles. So, according to this convention, the structures **1**, **2**, **3** and **4** may be called ZZ, EZ (two distinct conformers when $X \neq H$) and EE conformers of PSD and its derivatives. In a previous paper [19], a set of rules for an efficient nomenclature has been proposed to unambiguously distinguish these and other conformers. Same rules will also be used in this report. The extended sulfur diimides (as will be discussed in subsequent paragraph), may also be abbreviated with the same conventions.

The structures **5** and **6** in Fig. 1 are ZZ–ZZ and EE–EE conformers of (R^1(–N = S = N)–(N = S = N)–R^2) general formula. (There are numerous other possible conformers in this case that have been ignored in this study and will be discussed in detail in a future, more comprehensive report [22].) The same convention may be applied to structures **7** and **8** of (R^1(–N = S = N)$_3$–R^2) general formula (ZZ–ZZ–ZZ and EE–EE–EE conformers). Also, the structures **9** and **10** are perspectives of the long chains of connected PSD cores and may be termed (according to the number (k) of (–N = S = N–) groups involved) as $(ZZ)_k$ and $(EE)_k$ conformers. No claim has been made to whether these structures are the global minima on their PES, so their thermodynamic stability is not guaranteed.

As there is a large database of total electronic energies in this project, we have offered only the quantity "σ" as defined according to Eq. 1 to compact the tables in this paper:

$$\sigma = (E_e(X_0) + E_e(X_2))/2 - E_e(X_1). \qquad (1)$$

In this equation, E_e denotes the total electronic energy of corresponding optimized geometry whereas X_0 is the symbol for non-substituted (parent) molecules and X_1 and X_2 are the symbols for mono- and bi-substituted derivatives,

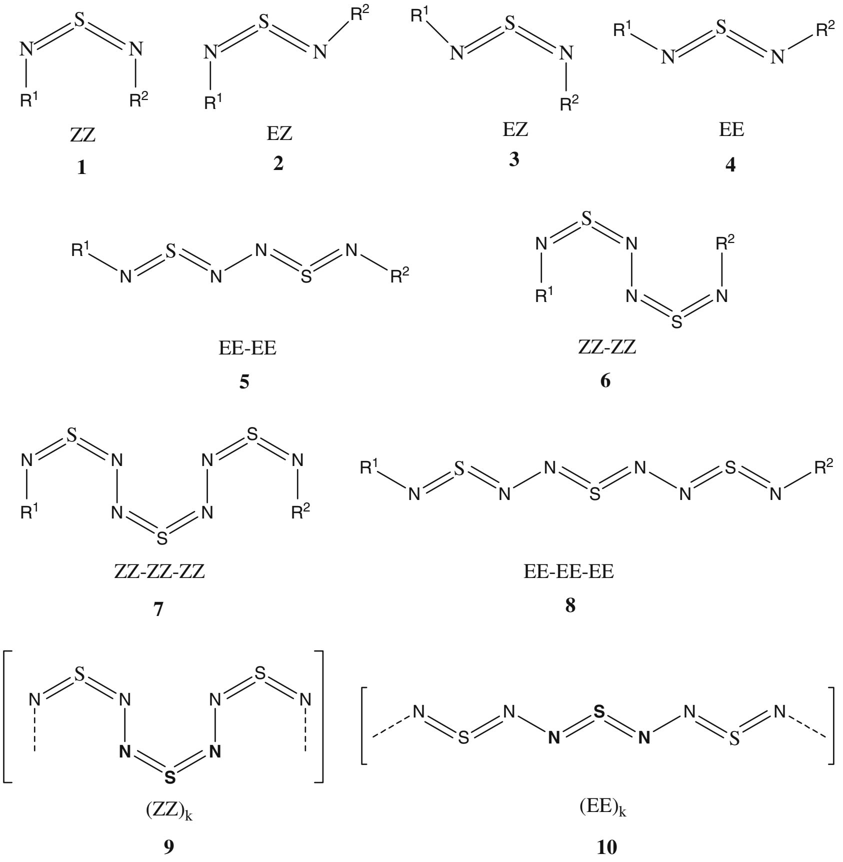

Fig. 1 The relevant conformers of parent and extended sulfur diimides employed in this study (see text for details)

respectively. Throughout this paper, this quantity has been computed only employing total energies of the "most" stable conformers of linear alkanes and their derivatives (to avoid confusion, the most stable conformer of each molecule has been indicated below the corresponding table) and has been offered in kcal mol^{-1}. In the ideal case, when the additive rule holds exactly for triple sets, σ will be zero; otherwise it is the measure for deviation from the additive rule (in this paper, we assume $\sigma < 2\,\text{kcal.mol}^{-1}$ as criteria for validity of an effective additive rule within chemical accuracy).

4 Additive rules

A large number of systems and also numerous methods and basis sets have been considered in this project, but only prototype examples will be discussed in the present report. We leave a more comprehensive presentation of geometric, energetic and also charge density topological characteristics to separate forthcoming paper [22]. To check the consistency with previous reports, σ has been offered for {H–CH$_2$–CH$_2$–H, H–CH$_2$–CH$_2$–R, R–CH$_2$–CH$_2$–R} triple sets with (R = OH, F, Cl) and also for the triple sets {H–(CH$_2$)$_3$–H, H–(CH$_2$)$_3$–R, R–(CH$_2$)$_3$–R} and {CH$_4$, CH$_3$R, CH$_2$R$_2$} with R = F in Tables 1, 2, 3, 4 and 5. As will be clarified further, reconsideration of these systems seems to be valuable.

Table 1 clearly demonstrates that in accord with previous report [11], the additive rule is indeed precise within chemical accuracy. Distribution of the values ($1.1 < \sigma < 1.7$) seems to be in a narrow range with least sensitivity to the level of calculation. So, one may look at the σ calculated (at HF/6-311++G(3df,2p) level) in the original paper (σ = 1.53) [11] as somewhere near the mean of this distribution This narrow distribution, clearly demonstrates that irrespective of the method and basis set employed for computations, the additive rule holds within chemical accuracy.

One must keep in mind that there are large differences between "mathematical structure" and "validity domain" of the methods used in this study. For instance, the efficiency of DFT-based exchange–correlation functionals commonly used in chemical literature varies considerably according to a recent comparative compendium (see [23] and references cited therein). On the other hand, the "BHandH" DFT method is based on a "non-optimized", arbitrary, combination of exchange (half of HF and half of local spin density exchange [24] functionals) and correlation (Lee, Yang and Parr's correlation functional [25,26]) functionals and so there is no a priori reason for its capability to maintain the delicate balance needed for an additive rule between total energies of triples considered in this paper. But, even this method works surprisingly well. As this insensitivity to the details of methods and basis sets used for calculations seems to hold for all

Table 1 The calculated σ values (kcal mol^{-1}) for species C_2H_6, C_2H_5F, FH_2CCH_2F

Basis set	Method								
	HF	BLYP	LSDA	MP2	B3LYP	LG1LYP	B3P86	BHandH	HCTH407
cc-pVDZ	1.38[a]	1.28	1.26	1.41[a]	1.35	1.36	1.35	1.42	1.26
cc-pVTZ	1.40	1.36	1.30	1.41	1.38	1.41	1.34	1.37	1.29
6-31G(d)	1.12[a]	1.13	1.11	1.14[a]	1.20	1.20	1.20	1.27	1.10
6-311+G(d,p)	1.59	1.63	1.51	1.61	1.61	1.67	1.55	1.57	1.51

All optimized structures have a staggered conformation

[a] The σ values have been computed employing anti (more stable) conformers of FH_2C-CH_2F molecule

Table 2 The calculated σ values (in kcal mol^{-1}) for species C_2H_6, C_2H_5Cl, ClH_2CCH_2Cl

Basis set	Method								
	HF	BLYP	LSDA	MP2	B3LYP	LG1LYP	B3P86	BHandH	HCTH407
cc-pVDZ	1.06	0.84	0.89	1.05	0.92	0.90	0.95	0.96	0.94
cc-pVTZ	0.94	0.79	0.86	0.94	0.85	0.83	0.85	0.89	0.82
6-31G(d)	1.05	0.93	0.95	1.04	0.98	0.98	0.96	1.00	0.98
6-311+G(d,p)	1.09	0.95	0.99	1.06	1.00	1.01	0.98	1.03	1.03

All species adapt anti conformation

Table 3 The calculated σ values (in kcal mol^{-1}) for species C_2H_6, $C_2H_5(OH)$ and $(OH)H_2CCH_2(OH)$

Basis set	Method								
	HF	BLYP	LSDA	MP2	B3LYP	LG1LYP	B3P86	BHandH	HCTH407
cc-pVDZ	0.17[a]	0.55[b]	0.60[b]	0.17[a]	0.55[b]	0.55[b]	0.55[b]	0.59[b]	0.58[b]
cc-pVTZ	0.33[a]	0.65[b]	0.78[b]	0.32[a]	0.65[b]	0.65[a]	0.66[b]	0.61[a]	0.69[b]
6-31G(d)	0.10[a]	0.55[b]	0.64[b]	0.09[a]	0.54[b]	0.54[b]	0.54[b]	0.54[c]	0.55[b]
6-311+G(d,p)	0.33[a]	0.52[d]	0.97[b]	0.51[e]	0.62[e]	0.70[a]	0.69[a]	1.10[e]	0.84[b]

[a] The σ values has been computed adapting the $C_2H_5(OH)$-anti(180) and $(OH)H_2CCH_2(OH)$-anti (180–180) conformations

[b] The σ values has been computed adapting the $C_2H_5(OH)$-anti(70) and $(OH)H_2CCH_2(OH)$-anti (70–70) conformations

[c] The σ values has been computed adapting the $C_2H_5(OH)$-anti(70) and $(OH)H_2CCH_2(OH)$-anti (180–180) conformations

[d] The σ values has been computed adapting the $C_2H_5(OH)$-anti(70) and $(OH)H_2CCH_2(OH)$-staggered (70–180) conformations

[e] The σ values has been computed adapting the $C_2H_5(OH)$-anti(180) and $(OH)H_2CCH_2(OH)$-staggered (70–180) conformations

cases considered in this paper (and also those that are calculated but not reported in this paper), the "physical" origin of additive rules must be something other than the method/basis sets' combinational efficiency to reconstruct the experimental thermodynamic data. This point will be considered further in the last section.

Tables 2 and 3 also demonstrate the same kind of insensitivity to the methods and basis sets employed in calculations. Distribution of σ values ($0.8 < \sigma < 1.1$ for Cl derivatives and $0.1 < \sigma < 1.1$ for OH derivatives) are also in the same narrow range as has been discussed in the case of fluorine derivatives. However, in accord with previous study [11], the overall σ values seem to be larger for fluorine derivatives. So, it seems that fluorine derivatives will be a more stringent test of the additive rule and subsequent tables are confined to the fluorine derivatives.

Tables 4 and 5 offer σ values for two other hydrocarbons, namely, methane and propane with their fluorine derivatives. In the case of methane triple set $\{CH_4, CH_3F, CH_2F_2\}$, distribution of σ values ($5.3 < \sigma < 9.1$) clearly shifts out of chemical accuracy range and one may safely deny the additive rule. On the other hand, in the case of propane triple set $\{H–(CH_2)_3–H, H–(CH_2)_3–F, F–(CH_2)_3–F\}$, distribution of σ values ($0.9 < \sigma < 1.1$) is within the chemical accuracy range and even the maximum error is lower than those of ethane and its derivatives' triple set ($1.1 < \sigma < 1.7$).

Table 6 offers corresponding σ values for the smallest member of sulfur diimide family, namely, PSD and its fluorine mono- and bi-derivatives. According to Fig. 1, different conformers seem to be plausible, but only the most stable conformer of each derivative and the parent molecule, namely, ZZ conformer (as stated in the table's footnote) has been used for calculating σ values. In this case, we are faced with a distribution of σ values ($3.9 < \sigma < 7.1$) such that it seems to be out of chemical accuracy range. Both qualitative and quantitative aspects of this distribution remind methane's triple set. To proceed further, only ZZ conformers of $R^1–(SN_2)_2–R^2$ and $R^1–(SN_2)_3–R^2$ hierarchies have been employed to calculate σ values. Previous experiences [17–22] make us confident regarding their stability relative to other possible planar conformers.

Tables 7 and 8 offer concise results. In both tables, one is faced with a narrow range of σ values, namely, $(0.1 < \sigma < 0.6)$ for $R^1–(SN_2)_2–R^2$ triple set (with two notable exceptions

Table 4 The calculated σ values (in kcal mol^{-1}) for species CH_4, CH_3F and CH_2F_2

Basis set	Method								
	HF	BLYP	LSDA	MP2	B3LYP	LG1LYP	B3P86	BHandH	HCTH407
cc-pVDZ	6.38	7.12	8.62	6.34	7.00	6.99	7.26	7.98	7.49
cc-pVTZ	6.14	6.40	7.84	6.09	6.39	6.36	6.66	7.45	6.98
6-31G(d)	6.99	7.52	9.05	6.95	7.45	7.37	7.81	8.43	7.96
6-311+G(d,p)	5.32	5.42	7.09	5.26	5.47	5.31	5.88	6.62	6.09

Table 5 The σ values (in kcal mol^{-1}) for species C_3H_8, $H_3C(CH_2)CH_2F$ and $FH_2C(CH_2)CH_2F$

Basis set	Method								
	HF	BLYP	LSDA	MP2	B3LYP	LG1LYP	B3P86	BHandH	HCTH407
cc-pVDZ	1.03	0.87	0.99	1.04	0.92	0.93	0.95	1.04	0.88
cc-pVTZ	0.99	0.94	1.04	0.99	0.97	0.98	0.97	1.05	0.91
6-31G(d)	1.02	0.88	1.00	1.04	0.93	0.93	0.95	1.03	0.88
6-311+G(d,p)	1.09	1.08	1.14	1.10	1.09	1.12	1.08	1.15	1.03

All species adapt anti conformation

Table 6 Computed σ values (in kcal mol^{-1}) for species HNSNH, HNSNF and FNSNF

Basis set	Method								
	HF	BLYP	LSDA	MP2	B3LYP	LG1LYP	B3P86	BHandH	HCTH407
cc-pVDZ	5.43	4.45	4.99	4.11	4.80	4.97	4.79	5.43	4.00
cc-pVTZ	5.05	4.39	4.74	4.35	4.67	4.80	4.63	5.15	3.89
6-31G(d)	5.29	4.03	4.40	4.27	4.46	4.61	4.45	5.07	3.68
6-311+G(d,p)	5.80	5.00	5.40	5.06	5.38	5.58	5.32	5.45	4.50

[MP2/cc-pVDZ (σ = 1.03) and MP2/6-31G(d) (σ = 0.75)] although none of them exceed σ = 2) and ($0.1 < \sigma < 0.3$) in the case of $R^1 - (SN_2)_3 - R^2$ triple set. Both these distributions are well within the range of chemical accuracy, like ethane and propane triple sets.

So, one may come to the conclusion that leave alone the smallest members of both series (namely, methane in alkanes and PSD in extended sulfur diimide series) additive rules hold for larger members of both series (and corresponding fluorine derivatives) irrespective of the method and basis set used in calculations.

5 Linear relations

To find out a complete correspondence with alkane series, checking a linear relation between the total energies of extended chains of sulfur diimides and the number of (–N=S=N–) units (n) seems desirable (in accord with the usual convention, we also define the number of (SN_2) units of a certain conformer by neglecting the (H–N=S=N–) moieties in the two ends of the corresponding conformer, so one must always keep in mind that "$n = k - 2$"). Indeed, previous independent theoretical investigations [5,12,27], as well as the comprehensive research program of Mosquera and co-workers [28–36], found linear relations between the total energies of numerous hydrocarbons and their derivatives against the number of their repetitive structural units. Accordingly, a recent investigation also demonstrates such a linear relation in a set of pure carbon-based nanotubes [37].

This study focuses on the extended chains of sulfur diimide family (see the sample structures **9** and **10** in Fig. 1). As there are numerous possible planar conformers for every member of extended sulfur diimide family (and the number of possibilities grows rapidly by addition of new (SN_2) units to the smaller chains [22]), only the $(ZZ)_k$ and $(EE)_k$ conformers have been selected for this study (as they are linear chains, one may extend them indefinitely). These two groups of conformers have been regarded as independent sets in subsequent mathematical operations.

The total electronic energies of optimized structures of $(ZZ)_k$ and $(EE)_k$ (k = 2–8 and 16 or alternatively n = 0–6 and 14) conformers as well as their energetic differences have been offered in Table 9. Linear regressions have been performed according to Eq. 2 employing different members of each set:

$$E_e(n) = a \times n + b. \tag{2}$$

In this equation, $E_e(n)$ denotes the total electronic energy of a conformer with n units of (SN_2) whereas a and b are regression parameters. These parameters, as well as the deviations from linear relation, all have been offered in Table 10. A detailed inspection of this table reveals interesting patterns. Although, regarding the absolute energies used for regression, the deviations seem to be negligible (only 0.001% in most stringent deviation), some of them seem to be out of chemical accuracy range (~1–2 kcal mol^{-1}). By employing all members of each set in regression process, one encounters the largest absolute mean and maximum errors as is evident from Table 10. So, some regressions were carried out by

Table 7 The computed σ values (in kcal mol^{-1}) for species HNSNNSNH, HNSNNSNF and FNSNNSNF

Basis set	Method								
	HF	BLYP	LSDA	MP2	B3LYP	LG1LYP	B3P86	BHandH	HCTH407
cc-pVDZ	0.16	0.24	0.29	1.03	0.22	0.22	0.23	0.26	0.22
cc-pVTZ	0.16	0.20	0.24	0.51	0.19	0.19	0.20	0.21	0.17
6-31G(d)	0.14	0.20	0.19	0.75	0.18	0.18	0.18	0.18	0.14
6-311+G(d,p)	0.14[a]	0.12	0.10	0.60[a,b]	0.12	0.14	0.12	0.14[a]	0.10

[a] The ZZ conformer of $(SN_2)_2FF$ molecule possesses one low imaginary frequency corresponding to out of plane deformation

[b] The ZZ conformer of $(SN_2)_2HF$ molecule possesses one low imaginary frequency corresponding to out of plane deformation

Table 8 The calculated σ values (in kcal.mol^{-1}) for species HNSNNSNNSNH, NSNNSNNSNF and FNSNNSNNSNF

Basis set	Method							
	HF	BLYP	LSDA	B3LYP	LG1LYP	B3P86	BHandH	HCTH407
cc-pVDZ	0.20	0.06[a,b]	0.10[a]	0.11	0.12	0.10	0.12	0.05
cc-pVTZ	0.13	0.08	0.09[a,b]	0.10	0.11	0.08	0.10	0.05
6-31G(d)	0.16	0.05[a]	0.08[a]	0.08	0.09	0.07	0.10	0.03
6-311+G(d,p)	0.09[b]	0.11[a]	0.11[a,b]	0.11	0.13	0.09	0.11[c]	0.06

[a] The ZZ conformer of $(SN_2)_3FF$ molecule possesseses one imaginary frequency

[b] The ZZ conformer of $(SN_2)_3HF$ molecule possesseses one imaginary frequency

[c] The ZZ conformers of $(SN_2)_3FF$ and $(SN_2)_3HF$ molecules possess two and one imaginary frequencies, respectively

Table 9 Total electronic energies of $(ZZ)_n$ and $(EE)_n$ (n = 0–6,14) conformers

Number of (SN_2) units, n	Total electronic energ (hartree)		Energy difference (kcal mol^{-1}), Δ
	ZZ	EE	
0	−1,016.470293	−1,016.439429	19.4
1	−1,524.096452	−1,524.062345	21.4
2	−2,031.730093	−2,031.700599	18.5
3	−2,539.370890	−2,539.347566	14.6
4	−3,047.016522	−3,046.996896	12.3
5	−3,554.664219	−3,554.647063	10.8
6	−4,062.312562	−4,062.297336	9.6
14	−8,123.506234	−8,123.502357	2.4

neglecting certain members of both sets. It was found (see Table 10) that the sole reduction of the number of conformers in regression process does not bring the results into chemical accuracy range. Only by discarding the smallest members of both sets, sharp reduction in both the absolute mean and maximum errors has been encountered. This clearly demonstrates that a slight (in absolute sense) but “systematic” (and important in chemical sense as will be discussed subsequently) deviation from the linear relation occurs for the smallest members of both sets.

To check this idea unambiguously, a new regression process has been conducted by including the three largest members of both sets (n = 5, 6 and 14). Although there is a large difference between the total electronic energies of these species, as is evident from Table 10, the final results (mean absolute deviations and maximum errors) appropriately position in the chemical accuracy range. On the other hand, the same table clearly offers the smooth convergence of regression parameters (a and b) employing larger members of both sets. So according to these results, we come to the conclusion that only by excluding the smallest members of both sets (n = 0, 1 and probably n = 2) a linear relation may be achieved within chemical accuracy (based on our experience regarding the regression process, we come to the conclusion that only a third -order polynomial is capable of reproducing the whole data set of Table 9 within chemical accuracy range). Table 11 offers the results of an independent test, namely, the predicted total electronic energies of $(ZZ)_{16}$ and $(EE)_{16}$ conformers employing Eq. 2 and the parameters of Table 10. It is evident from this table that the inclusion of smallest members of these sets in regression process causes significant “underestimation” of total energies of $(ZZ)_{16}$ and $(EE)_{16}$ conformers. Only neglecting the smallest members of both sets (n = 0, 1 and 2) makes it possible to have more reasonable estimates of total energies of the above-mentioned conformers. Accordingly, these results are also in line with previous conjecture based on the data of Table 10, and one may argue that the smallest members of both sets do not seem to participate effectively in linear relations. Table 12 offers the predicted total energies of the smallest members of both sets according to the regression parameters deduced from n = 5, 6 and 14 sets (assuming that this linear relation holds within chemical accuracy for more extended members of both sets). It is evident form this table that only for larger members ($n > 2$) the

Table 10 Regression results of total electronic energies for both $(ZZ)_n$ and $(EE)_n$ series

The members used for regression (n)	Regression parameters		Deviation (kcal mol^{-1})	
	a^a	b^a	Abs. mean	Maximum
$(ZZ)_n$				
0–6	−507.641028	−1,016.457065	4.41	8.30
0–5	−507.639161	−1,016.460176	3.84	6.35
0–4	−507.636690	−1,016.435550	3.29	4.28
2–6	−507.645827	−1,016.435550	1.24	1.81
3–6	−507.647271	−1,016.428327	0.43	0.56
4–6	−507.648020	−1,016.424334	0.09	0.14
5–6	−507.648343	−1,016.422504	–	–
5,6,14	−507.649150	−1,016.418091	0.18	0.27
$(EE)_n$				
0–6	−507.644266	−1,016.423092	4.95	10.25
0–5	−507.642537	−1,016.425974	4.74	8.44
0–4	−507.640016	−1,016.429336	4.42	6.33
2–6	−507.649297	−1,016.400704	0.54	0.82
3–6	−507.649948	−1,016.397451	0.15	0.22
4–6	−507.650220	−1,016.395998	0.01	0.01
5–6	−507.650273	−1,016.395698	–	–
5, 6, 14	−507.650603	−1,016.393891	0.07	0.11

[a] See Eq. 2 in the text

Table 11 The predicted total electronic energies of $(ZZ)_{16}$ and $(EE)_{16}$ conformers

The members used for regression (n)	Predicted total energ (hartree)		Deviation^a (kcal mol^{-1})	
	$(ZZ)_n$	$(EE)_n$	$(ZZ)_n$	$(EE)_n$
0–6	−8,123.431457	−8,123.442816	46.92	37.36
0–5	−8,123.408430	−8,123.421492	61.37	50.74
0–4	−8,123.377131	−8,123.389560	81.01	70.78
2–6	−8,123.477128	−8,123.490862	18.26	7.21
3–6	−8,123.490121	−8,123.496723	10.11	3.54
4–6	−8,123.496614	−8,123.499078	6.04	2.06
5–6	−8,123.499306	−8,123.499520	4.35	1.78
5, 6, 14	−8,123.506187	−8,123.502338	0.03	0.01

[a] See Table 9 for independently calculated total energies

Table 12 Predicted total electronic energies according to the regression parameters of n = 5, 6, 14 sets

n	Predicted total energy, (hartree)		Deviation^a (kcal mol^{-1})		Δ^b
	ZZ	EE	ZZ	EE	
0	−1,016.418091	−1,016.393891	32.76	28.57	15.19
1	−1,524.067241	−1,524.044494	18.33	11.20	14.27
2	−2,031.716390	−2,031.695098	8.60	3.45	13.36
3	−2,539.365540	−2,539.345701	3.36	1.17	12.45
4	−3,047.014690	−3,046.996304	1.15	0.37	11.54

[a] See Table 9 for independently calculated total energies

[b] Predicted relative energies (kcal mol^{-1}) of $(EE)_k$ and $(ZZ)_k$ conformers according to second and third columns of this table

chemical accuracy may be achieved within linear relation in both sets. Also from the same table and for the smallest members ($n \leq 2$) of both sets, the independently calculated total energies (see Table 9) indicate that they are more stable than the values predicted by a linear relation attained according to the total energies of more extended members of the sets considered. On the other hand, it seems that relative energies of similar members of both sets ($(ZZ)_k$ and $(EE)_k$) are less sensitive to the linear estimation method and so the predicted values in Table 12 are in semi-quantitative agreement with those obtained from direct calculations in Table 9. However, there are some minor but interesting differences that will be discussed in the next section.

So, one may come to the conclusion that leave alone the smallest members of both series (n = 0, 1 and probably 2), a linear relation between total electronic energies and the number of (SN_2) units holds for both $(ZZ)_k$ and $(EE)_k$ chains.

6 Conclusions and future prospects

The present study extends the recent research programs seeking additive rules and linear relation to extended sulfur diimide family. Indeed, there are additive rules and linear relation between total electronic energies of extended sulfur diimides and some of their derivatives. In this regard, some details are worth mentioning.

The observed insensitivity of additive rules to the method and basis sets employed in this study, as discussed in detail in Sect. 4, clearly demonstrates that the origin of additive rules must be something other than theoretical efficiency of a particular combination (method/basis set) to reconstruct the experimental data. So, these additive rules must be distinguished from those derived from thermodynamic compendiums. On the other hand, as in reliable reconstruction of experimental data, one must take into account the non-negligible contribution of some other energetic terms (like zero point energies, thermal effects and even possible statistical mixtures); the additive rules among theoretically derived total electronic energies must be classified separately. Although according to the present study we cannot trace the origin of these additive rules, it turns out that the satisfaction of a general stipulation by different methods and basis sets is probably the main driving force of these additive rules. (If such a general stipulation exists and is also satisfied by more realistic methods such as FCI/infinite basis set, then it will be safe to assume a single origin for both experimentally and theoretically observed additive rules.) It seems that more theoretical as well as computational studies are necessitated in order to shed some light on this enigma.

The observed deviations from linear relations for the smallest members of $(ZZ)_k$ and $(EE)_k$ chains as discussed in detail in Sect. 5 seem to be indications of a chemical “fine structure”. In this regard, the predicted energy differences based on regression parameters of more extended members of the above-mentioned sets are less than that derived from direct computation and this “extra” stability of (ZZ) conformer is in accord with our previous description [19,20, 22] of the strange “anti-steric” effect observed in the smallest members of these series. As has been stressed previously [19,20,22], there is unusual stabilizing electronic effect (termed “Z-effect”) in ZZ conformers of these smaller members and their derivatives. Indeed, comparison of the relative energies of $(ZZ)_k$ and $(EE)_k$ conformers according to Tables 9 and 12 demonstrates that in contrast to the smooth changes predicted by linear equation 2, energy differences calculated by direct computation are more pronounced for n = 0, 1, 2 cases. In direct ab initio computations, $(ZZ)_k$ conformers are predicted to be more stable than $(EE)_k$ by almost 4.2 (n=0), 7.1 (n=1) and 5.1 (n=2) kcal mol^{-1}. This “extra” stability of $(ZZ)_k$ conformers relative to $(EE)_k$ conformers may be regarded as quantitative manifestation of Z-effect (this point will be discussed more thoroughly in a subsequent publication [22]).

Although this study may be regarded as self-sustained, as discussed in first section, a QTAIM analysis will be helpful for a deeper insight of observed trends. Unfortunately in usual ab initio calculations, virial theorem is only satisfied approximately and as has been discussed recently [38], this causes serious drawbacks in energy decomposition of fragments. So, only state-functions derived from self-consistent virial scaling (SCVC) coupled with SCF procedure may be used for meaningful QTAIM analysis [39]. Unfortunately our efforts to construct SCVS-based state-functions on pre-optimized geometries failed and an effective scheme of SCVC calculations seems to be possible only with a renewed geometry optimization. So, we leave the QTAIM analysis within SCVS context to a forthcoming paper [40].

This study also indicates that searching the additive rules and linear relation for inorganic materials rewarding and, in long term, seems to be a promising research area.

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