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REGULAR ARTICLE

D. Barić · Z. B. Maksić

On the origin of Baeyer strain in molecules – an ab initio and DFT analysis

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Abstract It is shown that destabilization energy of organic molecules containing small rings can be estimated by quasi–homodesmotic reactions involving acyclic "strain–free" counterparts. These destabilization energies E_s can be well reproduced at the HF level employing cc-pVTZ basis set, because the contributions of the electron correlation and ZPV energy practically cancel each other in most cases. A predominating factor leading to a decreased stability of molecules involving small ring fragments is given by the Ω bond bending or Baeyer strain. It leads to a dramatic decrease in the electron–nuclei attraction, which is a hallmark of the angular strain. Similar results are obtained by the DFT–B3LYP method. It is strongly pointed out that Baeyer strain cannot be singled out from the total destabilization energy in a precise quantitative way, since it is interlocked with other types of intramolecular interactions like the nonbonded repulsions, a significant increase in the stability of the CH bonds emanating from the small cyclic structures and by the σ–aromaticity or σ–antiaromaticity in three– and four–membered rings, respectively. Nevertheless, it is fair to say that Baeyer strain is the essential factor in determining decreased stability of small ring compounds and that the diminished electron–nuclear attraction is its characteristic signature at the global level.

Keywords Strained ring · Angular strain · Baeyer strain · Bond bending

Dedicated to Professor Karl Jug on the occasion of his 65th birthday.

D. Barić · Z. B. Maksić
Quantum Organic Chemistry Group,
Department of Organic Chemistry and Biochemistry,
"Ruđer Bošković" Institute, POB 180,
10002 Zagreb, Croatia

Z. B. Maksić (✉)
Faculty of Science and Mathematics,
The University of Zagreb, Marulićev trg 19,
10000 Zagreb, Croatia
e-mail: zmaksic@spider.irb.hr

1 Introduction

The notion of strain energy is one of the concepts which evade the exact definition just like, for example, aromaticity and antiaromaticity, and yet are of immense importance in understanding chemical reactivity. It is not an observable property and cannot be defined as an expectation value of a quantum mechanical operator. In other words, it cannot be determined in a unique way. Rather, it can be stated that a strained compound is less stable than a reference "strain–free" system due to some unfavorable intramolecular interactions. It straightforwardly follows that strained species are more reactive as educts and less abundant as products. As early as 1885 it was realized by Alfred von Baeyer – a professor of organic chemistry at the University of Heidelberg – that small three– and four–membered ring compounds should be angularly strained, because their bond angles are smaller than ideal tetrahedral ones [1]. Since then, the angular or Baeyer strain was a subject matter of numerous studies [2] being a topic of all textbooks on chemistry. One way in estimating the strain energy in cycloalkanes, for example, would be to take cyclohexane as a strainless gauge molecule and to measure its heats of formation ΔH_f. It turns out that ΔH_f per CH_2 group is -4.92 kcal/mol. Hence the expected ΔH_f in cyclopropane is -14.75 kcal/mol. Since the measured ΔH_f value is 12.73 kcal/mol, one derives the angular strain of 27.5 kcal/mol. Analogously, the obtained strain energy in cyclobutane is 26.5 kcal/mol. This approach has two drawbacks: (1) cyclohexane is not a completely strain–free molecule and (2) the strain energy in cyclopropane and cyclobutane cannot be reduced to angular bending only, as one might wish (vide infra). Nevertheless, a ladder of strained molecules can be established in this way, which may well serve for comparative purposes. Franklin's group equivalents offer ΔH_f contributions for characteristic molecular fragments, which are very useful in this respect [4]. His scheme was extended and refined by other researchers [5, 6]. Although there are several types of unfavorable interactions leading to Pitzer torsional strain, Schoemaker–Dunitz nonbonded strain etc. [2], our focus in this paper will be on

Baeyer strain. It was realized by Coulson and Moffitt [7] more than 50 years ago that there is a close relation between the bent bonding and angular strain in cyclopropane. The simplest possible rationalization is given by the local hybrid orbitals. Two real hybrids formed by s and p AOs cannot form a mutual angle less than 90° (in which case they become pure p orbitals) implying that the so-called Ω bent bonds occur. Mårtensson and Öhrn [8] argued that complex AOs should be used in cyclopropane, since they could close an angle of 60°. However, it turned out that complex atomic hybrids (HAOs) have very poor overlapping and that the best HAOs are consequently real functions leading to displacement of the maximum electron density outside the CCC ring in cyclopropane [9]. The bent–bond description of small ring compound is a common knowledge nowadays [10,11]. A closely related interpretation of the angular strain energy was put by Siddarth and Gopinathan [12] based on the Jug and Gopinathan model of atomic valence strength [12,13], which is a generalization of the formalism introduced by Armstrong et al. [14]. An authoritative review on atomic valence in the molecular orbital theory can be found in Jug [15]. It turns out that atomic valence numbers in strained rings are invariably lower than in unstrained molecules. The increase in p–characters of HAOs describing strained small rings accompanied by a decrease in overlapping and atomic valence strengths provide a very simple and intuitively appealing rationalization at the local "microscopic" level. It is known, however, that the molecular strain is a collective feature [16], and consequently, it would be desirable to have at hand a global indicator of angular strain in compounds containing small ring(s). The present work shows that such an indicator is provided by the electron–nuclear attraction V_{eN} term. It can be safely stated that Baeyer strain in small ring systems originates from a decrease in V_{eN} attraction compared to acyclic components.

2 Theoretical model

Baeyer strain is considered here by the energy component analysis. For that purpose we shall employ the Hartree–Fock (HF) model, which will be complemented by the single–point MP2 [17] calculations in order to estimate the influence of electron correlation. Dunning's correlation consistent basis sets [18] are utilized. Systematic calculations on a large set of strained cyclic and polycyclic molecules were performed by applying cc-pVDZ and cc-pVTZ bases. However, in some test cases basis functions with higher angular momenta too were used. The zero point vibrational energies are computed at the HF level. The HF wave functions were constrained to satisfy virial theorem [19,20]. In addition, analysis of Baeyer strain was carried out by using density functional theory (DFT) [21,22] at the B3LYP [23,24] level for comparison. All calculations were executed by applying GAUSSIAN98 [25] code.

3 Results and discussion

The studied compounds are depicted in Fig. 1. Instead of using additivity schemes for ΔH_{f} in estimating strain energies E_{s}, we shall employ the concept of homodesmotic reactions introduced by George et al. [26]. They represent a useful vehicle in exploring the intramolecular interactions. These conceived reactions possess equal number of atoms of the same elements in reactants and products, which in turn are in the same canonical hybridization states. In addition, the number of single, double and triple bonds between the same atoms is preserved. The system of reactions providing a scale of strained compounds is given by Eqs. (1)–(20). It should be strongly pointed out that, strictly speaking, these reactions are not homodesmotic. The point is that CC bonds in strained rings possess HAOs with highly pronounced p–character, whereas the opposite holds for their CH bonds. Therefore, the s–characters of CC and CH bonds of small rings do not completely match hybridization in the corresponding bonds of the reference acyclic counterparts. For that reason it is better to characterize Eqs. (1)–(20) as quasi–homodesmotic. They can be used either for the ΔH_{f} values of the compounds in question, or for their total electronic energies (including the nuclear repulsion V_{NN} term).

$$\mathbf{1} + 3(\text{ethane}) = 3(\text{propane}) + E_{\mathrm{s}}(\mathbf{1}) \tag{1}$$

$$\mathbf{2} + 4(\text{ethane}) = 4(\text{propane}) + E_{\mathrm{s}}(\mathbf{2}) \tag{2}$$

$$\mathbf{3} + 5(\text{ethane}) = 5(\text{propane}) + E_{\mathrm{s}}(\mathbf{3}) \tag{3}$$

$$\mathbf{4} + 6(\text{ethane}) = 6(\text{propane}) + E_{\mathrm{s}}(\mathbf{4}) \tag{4}$$

$$\mathbf{5} + 6(\text{ethane}) = 4(\text{isobutane}) + E_{\mathrm{s}}(\mathbf{5}) \tag{5}$$

$$\mathbf{6} + 12(\text{ethane}) = 8(\text{isobutane}) + E_{\mathrm{s}}(\mathbf{6}) \tag{6}$$

$$\mathbf{7} + 5(\text{ethane}) = 2(\text{propane}) + 2(\text{isobutane}) + E_{\mathrm{s}}(\mathbf{7}) \tag{7}$$

$$\mathbf{8} + 6(\text{ethane}) = 3(\text{propane}) + 2(\text{isobutane}) + E_{\mathrm{s}}(\mathbf{8}) \tag{8}$$

$$\mathbf{9} + 6(\text{ethane}) = 3(\text{propane}) + 2(\text{isobutane}) + E_{\mathrm{s}}(\mathbf{9}) \tag{9}$$

$$\mathbf{10} + 6(\text{ethane}) = 4(\text{propane}) + (\text{neopentane}) + E_{\mathrm{s}}(\mathbf{10}) \tag{10}$$

$$\mathbf{11} + 9(\text{ethane}) = 3(\text{propane}) + 4(\text{isobutane}) + E_{\mathrm{s}}(\mathbf{11}) \tag{11}$$

$$\begin{aligned}\mathbf{12} + 12(\text{ethane}) &= 6(\text{propane}) \\ &\quad +3(\text{neopentane}) + E_{\mathrm{s}}(\mathbf{12})\end{aligned} \tag{12}$$

$$\mathbf{13} + 8(\text{ethane}) = 5(\text{propane}) + 2(\text{isobutane}) + E_{\mathrm{s}}(\mathbf{13}) \tag{13}$$

$$\mathbf{14} + 8(\text{ethane}) = 2(\text{propane}) + 4(\text{isobutane}) + E_{\mathrm{s}}(\mathbf{14}) \tag{14}$$

$$\mathbf{15} + 12(\text{ethane}) = 6(\text{propane}) + 4(\text{isobutane}) + E_{\mathrm{s}}(\mathbf{15}) \tag{15}$$

$$\begin{aligned}\mathbf{16} + 3(\text{ethane}) &= (\text{dimethylamine}) \\ &\quad +2(\text{propane}) + E_{\mathrm{s}}(\mathbf{16})\end{aligned} \tag{16}$$

$$\mathbf{17} + 3(\text{ethane}) = (\text{dimethylether}) + 2(\text{propane}) + E_{\mathrm{s}}(\mathbf{17}) \tag{17}$$

$$\begin{aligned}\mathbf{18} + 2(\text{ethane}) &= (trans - 2\text{-butene}) \\ &\quad +(\text{propane}) + E_{\mathrm{s}}(\mathbf{18})\end{aligned} \tag{18}$$

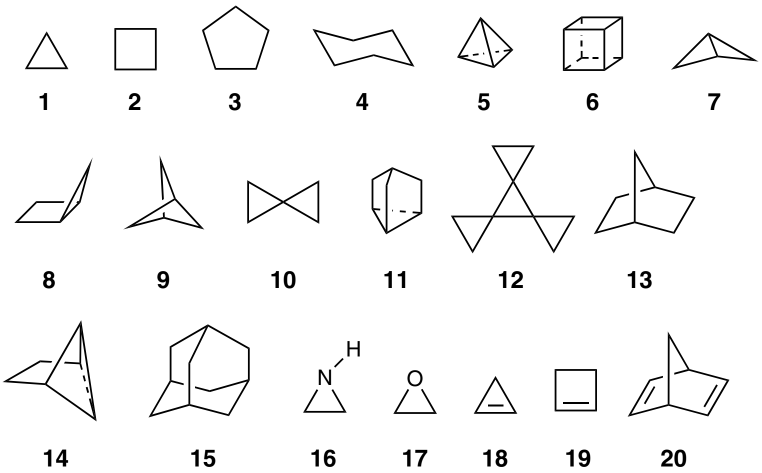

Fig. 1

$$\mathbf{19} + 3(\text{ethane}) = (trans - 2\text{-butene}) + 2(\text{propane}) + E_s(\mathbf{19}) \quad (19)$$

$$\mathbf{20} + 6(\text{ethane}) = 2(trans - 2\text{-butene}) + (\text{propane}) + 2(\text{isobutane}) + E_s(\mathbf{20}) \quad (20)$$

It was argued by Nelander and Sunner [27] that only electronic energy should be taken into account in calculation of the strain energies, since it is an intrinsic property solely of the electronic structure of strained molecules. Other terms like $ZPVE$ should be disregarded, since they do not depend on the angular strain. This conjecture is not quite justified. Although the $ZPVE$ is an additive property par excellence [28,29] within certain limits [30], it exhibits characteristic deviations from the additivity in highly strained rings, as the present results convincingly show. Consequently, we shall estimate the strain energies at the HF level first and discuss subsequently corrections due to the electron correlation and the $ZPVE$ effects.

We shall commence with the HF energy component analysis:

$$E(\text{HF}) = E(T) + V_{\text{ee}} + V_{\text{eN}} + V_{\text{NN}} , \quad (21)$$

where terms have their usual meaning. They satisfy the virial ratio $E(T)/[V_{\text{ee}} + V_{\text{eN}} + V_{\text{NN}}] = -0.5$. Survey of data presented in Table 1 yields several general conclusions. The strain energies calculated by the HF model E_s(HF) utilizing cc-pVDZ basis are in fair agreement with those estimated by the larger cc-pVTZ set, the latter being invariably lower. More pronounced differences are found in highly strained molecules involving two or more three–membered rings like, for example, in tetrahedrane **5**, bicyclo(1.1.0)butane **7**, spiropentane **10**, and polycyclopropylidene ([3]–rotane) **12**. It appears that the HF/cc-pVDZ model overshoots E_s(HF) in these molecules by 5.2, 2.9, 3.3 and 6.6 kcal/mol, respectively. In order to examine the influence of the basis set in determining HF strain energies, a number of calculations were carried out on the archetypal system **1** by employing cc-pVmZ ($m = 2, 3, 4, 5$) basis sets, where numbers $m = 2, 3, 4$ and 5 stand for DZ, TZ, QZ and 5Z functions. **It appears that E_s(HF) converges at the cc-pVTZ set** since changes induced by applying cc-pVQZ and cc-pV5Z bases are insignificant (Table 2). Taking into account E_s(MP2) strain energy calculated by the cc-pVTZ set and by substracting the $ZPVE$ contribution of -3.0 kcal/mol, one obtains $E_s(\mathbf{1}) = 27$ kcal/mol in excellent agreement with the experimental value (27.5 kcal/mol).

It is usually claimed that the angular strain energy is approximately additive in polycyclic rings. This seems to be the case for four–membered rings. Let us consider HF/cc-pVTZ results. According to the additivity rule E_s(HF) in cubane **6** should assume 156.0 kcal/mol, which compares with the actual calculation rather well (153.8 kcal/mol). However, additivity badly fails in molecules containing three–membered rings. For instance, the strain energies E_s(HF) in **5**, **7**, **10** and **12** are 133.2(106.4), 64.6(53.2), 57.8(53.2) and 120.1(106.4) kcal/mol, respectively, where the additivity values are given within parentheses, which means that the actual strain is significantly higher than the sum of E_s(HF) values of free rings. This is not surprising, since for example, in tetrahedrane **5** each carbon is a member of three cyclopropane rings at the same time. Consequently, the HAOs describing CC bonds belonging to two coalesced three–membered rings possess increased p–character ($sp^{4.1}$–$sp^{4.1}$) compared to that in cyclopropane **1** ($sp^{3.7}$–$sp^{3.7}$) and a higher Ω bond bending ($\delta = 30.2°$ vs. $\delta = 22.9°$) [31], which is the main cause of Baeyer strain. An increased strain in **7** is also expected in view of the fact that the perimeter bonds are not only bent, but twisted in addition. It was found by one of the present authors that the HAOs describing the side CC bonds pass by each other in space [32]. Moreover, the central CC bond is formed by $sp^{4.4}$–$sp^{4.4}$ hybrids, implying that its p–character is higher than that in tetrahedrane, whereas the side bond are

Table 1 The strain energy and its kinetic and potential components, as obtained by homodesmotic Eqs. (1)–(20), calculated at HF level of theory employing cc-pVDZ and cc-pVTZ basis sets (in kcal/mol)[a]

Equation	Basis set	ΔT	ΔV_{ee}	ΔV_{NN}	ΔV_{eN}	E_s(HF)	$\Delta(ZPVE)$	Δ(MP2)
(1)	DZ	−28.7	−28282.4	−28173.1	56512.7	28.5	−3.1	4.1
	TZ	−26.6	−28304.5	−28180.1	56537.9	26.6	−3.0	3.4
(2)	DZ	−27.2	−21265.9	−21265.9	42578.8	26.9	−2.6	2.1
	TZ	−26.0	−21306.0	−21299.3	42657.2	26.0	−2.6	2.5
(3)	DZ	−7.6	−8539.7	−8568.2	17122.7	7.2	−2.0	1.1
	TZ	−6.6	−8571.8	−8607.2	17192.1	6.6	−1.9	1.3
(4)	DZ	−1.3	8916.3	8906.6	−17820.6	0.9	−1.4	0.3
	TZ	−0.9	8937.3	8917.0	−17852.6	0.9	−1.4	0.4
(5)	DZ	−138.4	−112274.0	−111914.4	224465.2	138.4	−11.1	13.4
	TZ	−133.2	−112325.6	−111913.4	224505.4	133.2	−11.3	12.5
(6)	DZ	−156.5	−125915.9	−125920.5	252149.3	156.5	−13.6	19.1
	TZ	−153.8	−125898.8	−125916.2	252122.5	153.8	−14.0	19.2
(7)	DZ	−67.6	−66859.4	−66549.5	133544.1	67.5	−6.2	6.8
	TZ	−64.6	−66900.4	−66569.6	133599.3	64.6	−6.2	6.9
(8)	DZ	−55.6	−54540.1	−54392.9	109044.0	55.4	−5.5	6.8
	TZ	−53.2	−54582.5	−54427.1	109116.0	53.2	−5.5	6.7
(9)	DZ	−68.9	−52419.6	−52213.4	104770.6	68.7	−6.0	1.7
	TZ	−67.1	−52472.7	−52263.9	104870.6	67.1	−4.9	2.1
(10)	DZ	−61.4	−65543.8	−65319.6	130985.8	61.1	−6.1	10.1
	TZ	−57.8	−65551.1	−65313.6	130980.3	57.8	−6.2	10.6
(11)	DZ	−37.0	−56672.0	−56545.0	113290.7	36.7	−6.6	6.8
	TZ	−34.7	−56690.2	−56563.4	113322.9	34.7	−6.8	7.2
(12)	DZ	−127.1	−93732.3	−93266.3	18252.4	126.7	−12.3	21.3
	TZ	−120.1	−93524.1	−93047.2	186811.5	120.1	−12.8	22.7
(13)	DZ	−16.1	−9705.5	−9721.9	19459.4	15.8	−3.6	1.0
	TZ	−15.0	−9688.6	−9715.7	19434.3	15.0	−3.6	1.2
(14)	DZ	−69.6	−83532.3	−83305.0	166976.4	69.5	−8.1	10.4
	TZ	−66.3	−83587.3	−83343.0	167063.0	66.3	−8.3	10.3
(15)	DZ	−3.9	44704.7	44666.6	−86363.8	3.5	−4.2	1.1
	TZ	−3.8	44884.9	44823.3	−89700.6	3.8	−4.4	1.2
(16)	DZ	−25.6	−29007.0	−28862.4	57921.1	25.5	−3.1	2.1
	TZ	−23.9	−29028.4	−28875.2	57951.4	23.9	−3.1	2.5
(17)	DZ	−24.3	−29453.5	−29314.0	58815.9	24.1	−3.2	0.6
	TZ	−22.5	−29486.3	−29340.7	58872.0	22.2	−3.2	1.1
(18)	DZ	−56.3	−31360.8	−31211.4	62684.9	56.3	−3.4	1.0
	TZ	−54.4	−31374.6	−31217.2	62700.6	54.4	−3.4	1.5
(19)	DZ	−30.2	−25554.9	−25510.7	51126.0	30.2	−2.5	1.3
	TZ	−29.4	−25595.3	−25552.0	51206.2	29.4	−2.3	1.6
(20)	DZ	−31.5	−25909.8	−25873.0	51845.7	31.4	−3.4	−4.8
	TZ	−30.8	−25911.2	−25869.1	51841.9	30.8	−3.1	−4.2

[a] Δ denotes a contribution of a particular energy component to the strain energy according to quasi–homodesmotic reactions (1)–(20). The HF energy terms yield the strain energy E_s(HF) at the HF level. It should be corrected by the $ZPVE$ and electron correlation terms, $\Delta(ZPVE)$ and Δ(MP2), respectively

Table 2 Contributions of the kinetic and potential energy components to the HF strain energy of cyclopropane **1** calculated by the cc-pVmZ basis sets ($m = 2, 3, 4$ and 5), according to homodesmotic Eq. (1). In addition, the MP2 strain E_s(MP2) is given for comparison

m	ΔT	ΔV_{ee}	ΔV_{NN}	ΔV_{eN}	$E(\text{HF})_s$	E_s(MP2)
2	−28.7	−28282.4	−28173.1	56512.7	28.5	32.6
3	−26.6	−28304.5	−28180.1	56537.9	26.6	30.0
4	−26.5	−28340.5	−28217.5	56610.9	26.5	30.1
5	−26.4	−28314.6	−28186.9	56554.3	26.4	30.0

of $sp^{4.9}$–$sp^{3.7}$ composition [32]. Finally, in spiropentane **10** and [3]–rotane **12** it is found that the bond bending is larger than that in cyclopropane for the central C atoms [31,33]. It is useful to note in this respect that [3]–rotane **12** can be considered as system obtained by coalescence of three spiropentanes. Hence, if we take three E_s(**10**) energies diminished by two strain energies of cyclopropane, it follows that the strain energy of **12** is additive almost exactly. A simple counting of the strain energies of cyclopropane rings fails, however.

The largest strain is found in cubane **6** due to a large number of the four–membered rings. On the other hand, a strain–free molecule is effectively cyclohexane **4**. The next "strain–free" compound is adamantane **15** with its almost a perfect tetrahedral arrangement of covalent bonds, modest rehybridization of carbon atoms and negligible deviation of HAOs of −0.8° inside the six–membered rings [34].

Let us briefly consider the effect of electron correlation. For this purpose MP2(fc)/cc-pVmZ//HF/cc-pVmZ for m =

Table 3 The strain energies and their kinetic and potential components, for homodesmotic reactions (22)–(24), calculated at the HF/cc-pVDZ level of theory (in kcal/mol)

Equation	ΔT	ΔV_{ee}	ΔV_{NN}	ΔV_{eN}	E_s(HF)
(22)	−28.0	−32740.5	−32626.4	65423.0	28.0
(23)	−26.3	−27210.1	−27196.6	54459.2	26.3
(24)	−6.4	−15970.0	−15990.4	31973.2	6.4

Table 4 The strain energies and their kinetic and potential components, for homodesmotic equations (1)–(20), calculated at B3LYP/cc-pVDZ level of theory (in kcal/mol)

Equation	ΔT	ΔV_{ee}	ΔV_{NN}	ΔV_{eN}	E_s(B3LYP)
(1)	−29.1	−28412.3	−28315.9	56786.3	29.1
(2)	−26.8	−21423.2	−21419.8	42896.5	26.8
(3)	−7.8	−8696.7	−8727.5	17439.9	7.8
(4)	−1.8	8820.7	8810.0	−17627.1	1.8
(5)	−134.7	−112685.4	−112386.84	225341.5	134.7
(6)	−154.0	−126877.9	−126916.9	254102.9	154.0
(7)	−66.6	−67178.6	−66903.4	134215.2	66.6
(8)	−55.1	−54855.3	−54730.3	109695.9	55.1
(9)	−67.8	−52804.1	−52614.3	105554.1	67.8
(10)	−60.7	−65870.2	−65679.9	131671.6	60.7
(11)	−39.3	−57109.1	−57008.6	114196.3	39.3
(12)	−124.5	−94683.2	−94298.9	189231.0	124.5
(13)	−17.3	−9949.7	−9966.9	19951.2	17.3
(14)	−70.3	−84004.7	−83818.1	167963.5	70.3
(15)	−7.0	44350.7	44312.3	−88649.0	7.0
(16)	−25.8	−29232.5	−29131.1	58415.1	25.8
(17)	−23.2	−29666.9	−29579.1	59292.4	23.2
(18)	−55.4	−31515.3	−31374.4	63000.6	55.4
(19)	−30.1	−25672.1	−25631.5	51363.8	30.1
(20)	−31.1	−26240.3	−26200.6	52503.2	31.1

2, 3, 4 and 5 are performed on the archetypal cyclopropane **1** (Table 2). **We would like to reiterate that convergence of MP2 strain energies E_s(MP2) is achieved for cc-pVTZ basis set, which is gratifying indeed**. Inspection of the results in Table 1 shows that E_s(MP2) is generally larger than E_s(HF). Therefore, it is safe to conclude that **the larger strain, the higher electron correlation effect, as evidenced by compounds 5, 6 and 12**, which is an important finding. This feature is in harmony with our recent results that the correlation energy in strained small rings is lower than that estimated by the additivity rule [35]. In other words, the electron correlation does not stabilize the bent bond as much as the axially symmetric σ-bond. This can be rationalized by the fact that the electron density is dispersed over a larger portion of the 3D space in strained compounds due to bent bonding. Hence, the electron correlation corrections to the diffused HF electron distributions is smaller than in the electronically congested systems like, for example, in HO–OH, O_3 etc.

In contrast, the zero point vibrations decrease the angular strain. A plausible explanation would be that the strained CC bonds are weaker, because of bent bonding, thus leading to lower vibrational energies. It is taken for granted here that the CH bond stretching frequencies increase due to the rehybridization effect, but they cannot completely compensate for a decrease in the CC vibrational energy. Naturally, the $ZPVE$ effect is more pronounced in highly strained molecules like, for example, in **5**, **6**, **12** and **14** (Table 1). It follows as an important corollary that **the electron correlation and $ZPVE$ effect cancel to a large extent in most cases**. Consequently, the HF model appears to be a reasonable approximation in calculating the angular strain energies provided cc-pVTZ basis set is employed. In accurate estimates both correlation and $ZPVE$ effects should be accounted for.

Although it is quite clear that Baeyer strain can be reduced to a decreased overlapping in the bent bonds and useful empirical bilinear least square fit relation exists between destabilization energies and CC $\sigma-$ and $\pi-$overlap integrals [36,37], the HF energy decomposition analysis is illuminative. Examination of ΔT, ΔV_{ee}, ΔV_{NN} and ΔV_{eN} contributions to E_s(HF) given in Table 1, where Δ denotes a contribution to the strain energy E_s(HF), reveals that it is a decreased electron–nuclei attraction, which results in Baeyer strain. A shift of the electron density from the center of the covalent CC bonds off the straight line connecting linked nuclei obviously leads to a lower V_{eN} attraction. The present calculations convincingly show that **a low V_{eN} is the prime cause and signature of the angular strain at the global level**. It is remarkable that all three terms ΔV_{ee}, ΔV_{NN} and ΔV_{eN} change sign in strainless compounds **4** and **15**. A decrease in V_{eN} term is dramatic in all strained systems. For example, ΔV_{eN} in **1**, **5** and **6** is 56537.9, 224505.4 and 252122.5 kcal/mol, respectively, as computed by the HF/cc-pVTZ model. These huge numbers are curtailed by the strongly favored V_{ee} and V_{NN} interactions in strained molecules. Finally, a modest but important stabilization of small strained cyclic and polycyclic compounds arises from the kinetic energy. **It follows that customary "small" Baeyer strain energies are results of an interplay of very large numbers**.

It is interesting to point out that there is not a good quantitative correlation between V_{eN} term and the resulting strain energies $E_{\mathrm{s}}(\mathrm{HF})$, in spite of the fact that the former exerts the overwhelming effect. There is a good reason behind that. Let us consider cyclopropane **1** in some more detail. Closure of the three–membered ring is accompanied with rehybridization which weakens the CC and strengthens CH bonds. The latter stabilize the molecule to a significant extent as discussed in the literature by several authors [39,40,41,42]. It is a consequence of the substantial redistribution of the s-character from the CC to CH bonds, which subsequently leads to considerably better overlapping between the hybrids and 1s(H) AOs [11]. As a result, the bond dissociation energy of the CH bonds in ethylene and cyclopropane are quite close. In other words, the true angular strain of the cyclopropane ring is higher than the apparent $E_{\mathrm{s}}(\mathbf{1})$ value. However, methylene groups are also eclipsed at the same time, which leads to some repulsion. There is another very interesting phenomenon described by Dewar [38] taking place in cyclopropane. Dewar showed that bent HAOs in **1** were delocalized leading to aromatic stabilization in full analogy with π–electron AOs in benzene. This effect was reexamined by Cremer and Gauss [16], who ascribed an amount of 17 kcal/mol to the surface delocalization of two σ–electrons delocalized over three carbon atom centers, which should be considered as a lower bound to the σ–aromaticity. Taking into account all intramolecular interactions in **1**, Cremer and Gauss concluded that its Baeyer strain should be about 41 kcal/mol or higher [16]. This is considerably larger than $E_{\mathrm{s}}(\mathrm{HF})$ estimated by the quasi–homodesmotic reaction (1), but, even this estimate should be taken *cum grano salis*, since the role of the σ–delocalization in **1** was questioned by some authors [43,44]. Nevertheless, the σ–aromaticity is definitely present in **1** and it was confirmed more recently by the negative nucleus independent chemical shifts (NICS(1)) calculated 1 Å above the center of cyclopropane ring [45], by a large diamagnetic susceptibility and its considerable anisotropy [46] and, last but not least, by an upfield ^{1}H NMR chemical shift [47]. It appears that Baeyer strain is intermingled with other intramolecular de/stabilization interactions implying that it is impossible to extract a precise value of the angular strain in an unambiguos way. Similarly, cyclobutane **2** should be σ–antiaromatic. This seems to be the case indeed according to NICS(1) value calculated by Exner and Schleyer [45]. The presence of the antiaromatic destabilization in **2** means that Baeyer strain should be smaller than that obtained by Eq. (2). It follows as a bottom line that **Baeyer strain cannot be accurately determined by the quasi–homodesmotic reactions (1)–(20), since it is interlocked with other types of the intramolecular nonbonded interactions, and/or by the anti/aromaticity of the σ–electrons describing the CC bonds of a small ring. However, it is beyond any reasonable doubt that Baeyer strain is an essential part of $E_{\mathrm{s}}(\mathrm{HF})$ and that its origin stems from the dramatic decrease in the electron–nuclear attraction term in molecules containing small ring fragments**.

Another possibility of "measuring" Baeyer strain would be to use cyclohexane as a "strain–free" gauge molecule. Indeed, **4** has a practically vanishing angular strain and the corresponding quasi–homodesmotic reactions for **1**, **2** and **3** take a form:

$$2(\text{cyclopropane}) = (\text{cyclohexane}) + 2E_{\mathrm{s}}(\mathbf{1})' \qquad (22)$$

$$3(\text{cyclobutane}) = 2(\text{cyclohexane}) + 3E_{\mathrm{s}}(\mathbf{2})' \qquad (23)$$

$$6(\text{cyclopentane}) = 5(\text{cyclohexane}) + 6E_{\mathrm{s}}(\mathbf{3})' \qquad (24)$$

The strain energies calculated by the HF/cc-pVDZ model $E_{\mathrm{s}}(\mathbf{1})'$, $E_{\mathrm{s}}(\mathbf{2})'$ and $E_{\mathrm{s}}(\mathbf{3})'$ are presented in Table 4. They are 28.0, 26.3 and 6.4 kcal/mol correspondingly thus being in excellent agreement with results obtained by Eqs. (1)–(3) treated at the same theoretical level. Therefore, despite the fact that the quasi–homodesmotic reactions (22)–(24) are more acceptable from the conceptual point of view, they offer practically the same results for the first members of the cycloalkane family of compounds.

In view of a wide popularity of the B3LYP method in chemistry, we performed calculations of the strain energies of compounds **1**–**20** employing quasi–homodesmotic reactions (1)–(20) and the cc-pVDZ basis set. The numerical data are summarized in Table 4. A comparison with the HF/cc-pVDZ strain energies presented in Table 1 reveals good agreement. Perusal of the results shows that the origin of the angular strain destabilization is again the unfavorable electron–nuclei attraction in molecules involving small ring(s). Therefore, in spite of some small numerical differences, all general conclusions remain the same. It follows that the strain energies of pure hydrocarbons are not very sensitive on the choice of the quasi–homodesmotic reactions (acyclic alkanes vs. cyclohexane), selection of the method (HF vs. B3LYP) and employment of different basis sets (cc-pVDZ vs. cc-pVTZ). However, the latter (cc-pVTZ) set should be preferred, since it represents the best compromise between accuracy and practicality.

4 Concluding remarks

We have convincingly shown that:

(1) Baeyer strain is a dominating factor leading to a decreased stability of molecules containing small ring(s). The latter is very well reproduced by the HF model employing a modest cc-pVTZ basis set and a reasonably well-selected system of quasi–homodesmotic reactions. The $ZPVE$ and correlation energy effects are of the opposite sign and cancel to a large extent in most cases. The B3LYP method yields closely similar results to the HF model provided the same basis set is applied. It should be kept in mind that Baeyer strain itself cannot be quantitatively estimated even within a system of carefully selected quasi–homodesmotic reactions, since it is "contaminated" by

other types of the strain destabilization energies like nonbonded interactions, by stabilizing effects such as increased strength of the CH bonds, or by the σ–aromaticity and σ–antiaromaticity occurring in the three– and four–membered rings, respectively.

(2) It is found that the electron–nuclei attraction energy V_{eN} term is a signature of Baeyer strain at the global level. It is dramatically decreased in compounds containing small ring(s).

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