The Baeyer strain is strongly affected by the nucleus–electron attraction—a comment on the Letter of G. Hohlneicher and L. Packschies [Tetrahedron Lett. 2007, *48*, 6429–6433]

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Abstract

The origin of the angular strain is studied in deformed methane and cyclohexane selected as the model systems par excellence. It is shown that the electron correlation contribution to the angular strain is negligible. Analysis of the Hartree–Fock energies provides a convincing evidence that the angular strain is a consequence of the unfavourable nucleus–electron attraction occuring due to bond bending. This should take place in other angularly distorted molecules as a rule. However, other effects might be even more important sometimes. In these cases the V_{ne} term can serve as a useful diagnostic tool.
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Recently, we analyzed the angular strain energy in a number of small ring compounds.[1] For that purpose, we utilized customary homodesmotic reactions.[2] Typical examples related to the first four cycloalkanes **m** (**m** = **1** − **4**) are given by equations:

$$\mathbf{m} + n(\text{ethane}) = n(\text{propane}) + E_s(\mathbf{m}) \qquad (1)$$

where *n* is the number of the carbon atoms ($n = \mathbf{m} + 2$). It was shown that the destabilization energies E_s could be well reproduced by the HF/cc-pVTZ model, because the contributions of the electron correlation and *ZPV* (zero point vibration) energy cancelled to a great deal in most cases. Subsequently, we examined the change in the HF potential energy between 'reactants' and 'products' in Eq. 1 yielding

$$E_s(\mathbf{m}) = E_{HF}(\mathbf{m}) - n[E_{HF}(\text{propane}) - E_{HF}(\text{ethane})] \qquad (2)$$

The term within the square parentheses defines the reference (i.e., the energy of the 'strainless' CH_2 group) in estimating the strain energy of systems involving small rings.

This widely accepted approach is in principle equivalent to an alternative gauge for determining strain energies, given by the heats of formation additivity schemes.[3,4] The difference in the HF energies in Eq. 2 can be resolved using the usual components:

$$\Delta E_{HF}(\mathbf{m}) = 1/2[\Delta V_{ee}(\mathbf{m}) + \Delta V_{ne}(\mathbf{m}) + \Delta V_{nn}(\mathbf{m})] \qquad (3)$$

The virial requirement is imposed here and the symbols have obvious meaning. It was found that the difference $\Delta V_{ne}(\mathbf{m})$ is indicative of the angular strain destabilization energy. The change in nucleus–electron interaction is positive in the strained carbocles **m** (**m** = **1** − **3**) starting with cyclopropane (**m** = **1**), being negative in cyclohexane **4**, which is an almost strain free molecule. The unfavorable nucleus–electron attractions in cyclopropane, cyclobutane, and cyclopentane (**m** = **1** − **3**) are in accordance with the bent CC bond concept[5–7] and intuitive notion that the off-center concentration of the electron density will diminish its attraction to the directly bonded atoms. Clearly, bent bonding also leads to decreased overlapping, which implies diminished exchange interaction. Therefore, it came as no surprise that a good description was found between the overlapping of local hybrid AOs and the 'experimental'

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strain energies.[8,9] It is concluded that overlapping provides 'microscopic' indicators, whereas the ΔV_{ne} term offers a qualitative global index of the angular strain.[1] It should be strongly pointed out that a *caveat emptor* was issued at the same time, by stating that Baeyer strain is just one part of the (un)favorable intramolecular interactions and that there is no direct correlation between the ΔV_{ne} term and the total destabilization energies.[1]

Hohlneicher and Packschies[10] challenged the idea that the contribution of the ΔV_{ne} term in determining the angular strain is important claiming that it was erroneous instead. This controversy requires resolution. We shall not dwell on the flaw such as the assertion that the aromaticity is observable, whereas the angular strain is not,[10] since it is clear by now that both features cannot be defined in a unique way. However, we would like to emphasize that our Letter was seriously misinterpreted by a statement that the correlation effects in Eq. 1 were of minor importance 'due to a strong cancellation of static and dynamic correlation'.[10] The matter of the fact is that these two kinds of correlation energy were not considered by us at all.[1] Instead, the total correlation energy was estimated at the MP2 level.[11]

To show that the ΔV_{ne} interaction does affect the angular strain, we examined two characteristic types of the deformed tetrahedral C atom in chemical environments. The first has C_{2v} local symmetry as in cyclopropane, whereas the second exhibits C_{3v} symmetry, as in tetrahedrane. The model systems are given by C_{2v} (Fig. 1a) and C_{3v} (Fig. 1b) deformed methanes. Let us focus on the C_{2v} case first. The angle θ is parametrically varied in the range of 100–140°. The rest of the structural parameters were optimized at the HF level. The destabilization energy upon distortion is calculated by the formula $E_s(\text{methane})_{C_{2v}} = \Delta E(\text{methane})_{C_{2v}} = E(\text{methane})_{C_{2v}} - E(\text{methane})_{T_d}$. The Hartree–Fock energies are calculated by Dunning's cc-pVmZ (m = D, T, Q and 5) correlation consistent basis sets.[12] The changes in the correlation energies are estimated by Grimme's SCS-MP2 approach based on the separate scaling of parallel and antiparallel spin-pair contributions.[13] Specifically, they are obtained by the single-point SCS-MP2(fc)/cc-pVmZ//HF/cc-pVmZ calculations. The results are summarized in Table 1. Perusal of the data shows that the results are practically converged at the cc-pVTZ basis set. Further, they reveal that the origin of the strain energy is given by the increased ΔV_{ne} term, which assumes positive values. In contrast, all the other terms are decreased. This holds for both smaller θ, less than tetrahedral angle (θ = 100°) and larger θ values
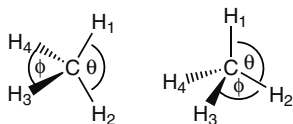

Fig. 1. Two types of methane distortions conforming to C_{2v} and C_{3v} symmetries, respectively.

Table 1
The HF energies and their components of the deformed methane relative to the equilibrium CH_4 structure according to the formula $E_{HF}(\text{methane})_{C_{2v}} = E_{HF}(\text{methane})_{T_d} + \Delta E(\text{methane})_{C_{2v}}$ calculated from various basis sets

θ (°)	ϕ (°)		cc-pVDZ	cc-pVTZ	cc-pVQZ	cc-pV5Z	$\delta(\theta')$	$\delta(\phi')$
100	111.7	$\Delta E^{(HF)}$	1.5	1.5	1.5	1.5	8.1	−0.8
		ΔT	−0.9	−3.5	−3.6	−3.6		
		ΔV_{ee}	−0.2	−4.9	−5.1	−5.2		
		ΔV_{nn}	0.6	−4.6	−4.8	−4.9		
		ΔV_{ne}	2.0	14.5	15.0	15.2		
		$\Delta E^{(MP2)}$	1.4	1.3	1.3	1.6		
120	107.1	$\Delta E^{(HF)}$	1.7	1.8	1.8	1.8	−8.9	0.8
		ΔT	−1.2	−3.8	−3.9	−3.9		
		ΔV_{ee}	−0.2	−5.1	−5.3	−5.4		
		ΔV_{nn}	0.5	−4.8	−5.0	−5.1		
		ΔV_{ne}	2.6	15.4	15.9	16.1		
		$\Delta E^{(MP2)}$	1.9	1.6	1.6	1.6		
130	104.8	$\Delta E^{(HF)}$	6.5	6.5	6.5	6.5	−17.0	1.5
		ΔT	−5.3	−8.7	−8.6	−8.7		
		ΔV_{ee}	−2.6	−8.2	−8.5	−8.7		
		ΔV_{nn}	−0.3	−6.1	−6.3	−6.5		
		ΔV_{ne}	14.7	29.6	30.0	30.3		
		$\Delta E^{(MP2)}$	5.9	5.9	5.9	5.9		
140	102.5	$\Delta E^{(HF)}$	13.9	14.1	14.1	14.1	−24.8	2.2
		ΔT	−11.6	−16.5	−16.1	−16.2		
		ΔV_{ee}	−5.9	−12.9	−13.3	−13.6		
		ΔV_{nn}	−1.4	−8.2	−8.5	−8.7		
		ΔV_{ne}	32.9	51.6	52.0	52.5		
		$\Delta E^{(MP2)}$	12.7	12.7	12.6	12.6		
145	101.4	$\Delta E^{(HF)}$	18.6	18.8	18.8	18.8	−28.7	2.4
		ΔT	−15.6	−21.3	−20.8	−20.9		
		ΔV_{ee}	−7.7	−15.6	−16.2	−16.5		
		ΔV_{nn}	−2.0	−9.4	−9.8	−10.0		
		ΔV_{ne}	43.9	65.2	65.6	66.2		
		$\Delta E^{(MP2)}$	17.0	16.9	16.9	16.8		

The $\Delta E^{(MP2)}$ change is obtained by the spin-component scaled MP2 (see text). θ and ϕ are bond angles, whereas the corresponding interhybrid angles are denoted by a prime. Bond bending is given by $\delta(\theta') = \theta - \theta'$ and $\delta(\phi') = \phi - \phi'$.

(θ = 120–145°). Secondly, the electron correlation energy $\Delta E(\text{corr}) = \Delta E(\text{HF}) - \Delta E(\text{MP2})$ contribution is very small and negative. It is interesting to observe that the change in the correlation energy is 1/10 of the change in the HF energy taken with the opposite sign. Hence, the correlation energy is slightly increased in the deformed structure. A rationale is given by the fact that if the interhybrid angle is smaller than tetrahedral, then the corresponding HCH segment becomes congested and the correlation is more important. The next step is to show that the reason behind the destabilization of $\Delta E(\text{methane})_{C_{2v}}$ is the bond bending. Wiberg[14] was the first to realize that the CH bonds should be bent because the hybrid AOs follow the bond bending vibrations to a very limited extent. For that purpose we calculated the NBO hybridization indices,[15] which are presented in Table S1 of Supplementary data, using the HF/cc-pVTZ model. The interhybrid angles are denoted by θ' and ϕ'. The differences $\delta(\theta') = \theta - \theta'$ and $\delta(\phi') = \phi - \phi'$ give the extent of the bond bending of the two CH bonds

closing the angle θ or ϕ. The positive values indicate the outside bending, whereas the opposite holds for negative δ. The bending angles $\delta(\theta')$ and $\delta(\phi')$ are given in the last two columns of Table 1. The calculated deviation angles are interesting. For instance, the $\delta(\theta')$ values for the imposed angles 100° and 120° are 8.2° and −9°, respectively. On the other hand, the optimized angle ϕ assumes correspondingly the values of 111.7° and 107.1°. The respective deviation angles $\delta(\phi')$ are −0.8° and 0.8°. Therefore, the bond angles tend to be as close to the tetrahedral values as possible and the bond bending as minimal as possible to ensure maximal overlapping. This is in harmony with the hybridization model and its success in describing local molecular properties.[16,17] It is noteworthy that the orthogonality requirement for the local hybrid orbitals leads straightforwardly to the conclusion that closing up of the angle θ' implies opening of the angle ϕ' and vice versa.[18] The same holds for the corresponding bond angle, which is known experimentally as the Thorpe–Ingold effect.[19] It is important to stress that bond bending rapidly increases, if the deformation is enhanced. For example, for $\theta = 140°$ the bending angle $\delta(\theta')$ is −24.8°. At the same time, the corresponding angles ϕ and ϕ' are 102.5° and 104.7°, respectively, implying deviation $\delta(\phi')$ of only 2.2°. This means that the HCH angle ϕ is predominantly determined by the angle of the corresponding hybrid AOs. It is also remarkable that the hybrid s-characters do not dramatically change around the tetrahedral 25% value (Table S1). This finding explains the very small change in the correlation energy upon distortion. The most important outcome is that the angular strain is considerably increased

Table 2
The HF energies and their components of the C_{3v} deformed methane relative to the equilibrium CH_4 structure according to the formula $E_{HF}(\text{methane})_{C_{3v}} = E_{HF}(\text{methane})_{T_d} + \Delta E(\text{methane})_{C_{3v}}$ calculated from various basis sets

θ (°)	ϕ (°)		cc-pVDZ	cc-pVTZ	cc-pVQZ	cc-pV5Z	$\delta(\theta')$	$\delta(\phi')$
100	117.1	$\Delta E^{(HF)}$	6.5	6.6	6.6	6.6	15.6	−5.0
		ΔT	−5.0	−8.7	−8.7	−8.8		
		ΔV_{ee}	0.4	−5.7	−6.0	−6.1		
		ΔV_{nn}	3.0	−3.3	−3.5	−3.6		
		ΔV_{ne}	8.1	24.4	24.8	25.1		
		$\Delta E^{(MP2)}$	5.9	5.8	5.8	5.8		
120	97.2	$\Delta E^{(HF)}$	9.4	9.5	9.5	9.5	−8.2	9.9
		ΔT	−7.3	−11.6	−11.5	−11.6		
		ΔV_{ee}	−0.9	−7.1	−7.4	−7.5		
		ΔV_{nn}	4.1	−2.4	−2.6	−2.7		
		ΔV_{ne}	13.5	30.6	30.9	31.3		
		$\Delta E^{(MP2)}$	8.5	8.5	8.5	8.5		
130	83.1	$\Delta E^{(HF)}$	38.1	38.4	38.4	38.4	−16.3	21.8
		ΔT	−30.8	−41.3	−40.6	−40.7		
		ΔV_{ee}	−13.0	−24.8	−25.5	−27.2		
		ΔV_{nn}	13.2	2.3	1.7	0.5		
		ΔV_{ne}	68.7	102.0	102.7	108.2		
		$\Delta E^{(MP2)}$	34.5	34.6	34.5	34.4		

All labels have the same meaning as in Table 1.
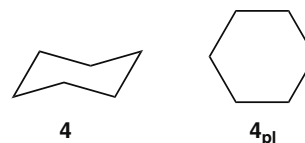
Fig. 2. Schematic representation of cyclohexane **4** and its planar from **4**$_{pl}$.

by the more pronounced bending in parallel with the increased V_{ne} interaction term (Table 1).

A similar situation is found for the C_{3v} distortion (Table 2). A notable difference is that once the deformation angle θ is fixed, the counterpart angle ϕ is determined by symmetry too. This has an important consequence that ϕ does not have a variational freedom and concomitant deviation angles $\delta(\phi')$ are highly pronounced in strongly deformed geometries. It is, therefore, not surprising that the angular strain is much larger as it is, for example, in the well-known molecule tetrahedrane. Specifically, for $\theta = 130°$ the angle ϕ assumes 83° and the deviations $\delta(\theta')$ and $\delta(\phi')$ are −32.6° and 21.8°, respectively. Not unexpectedly, the angular strain increases to 38.4 kcal/mol. Once again, the correlation effect is approximately one tenth of $\Delta E(HF)$ with the opposite sign. The ΔV_{nn} term is small and positive ranging from 2.3 (cc-pVTZ) to 0.5 (cc-pV5Z) kcal/mol (basis set) in this particular case ($\theta = 130°$) being negative otherwise. The overwhelming influence in all deformed structures is exerted by the nucleus–electron ΔV_{ne} term, which is always large and positive, thus proving our point.

The bottom line is that in CH_4, deformed tetrahedral structures of C_{2v} and C_{3v} symmetries are less stable than the equilibrium T_d geometry due to unfavorable nucleus–electron attraction calculated at the HF level. The correlation energy contribution is negative being roughly (1/10) of the $\Delta E(HF)$ energy difference in absolute value. It is important to emphasize that deformed C_{2v} and C_{3v} methanes are clear cut cases, where other effects usually occurring in strained cyclic molecules (vide infra) are absent.

Table 3
Values of $\Delta E_{HF}(\text{cyclohexane})_{D_{6h}}$ obtained from the equation $\Delta E_{HF}(\text{cyclohexane})_{D_{6h}} = E_{HF}(\text{cyclohexane})_{D_{6h}} - E_{HF}(\text{cyclohexane})_{opt}$ and their components as computed by the HF/cc-pVTZ model (in kcal/mol)

θ (°)	ΔT	ΔV_{ee}	ΔV_{nn}	ΔV_{ne}	$\Delta E(HF)$	$\Delta E(MP2)$
106.5	−32.3	−4231.4	−4332.2	8624.4	28.5	28.5
110	−35.2	−4308.7	−4422.9	8797.8	31.1	30.8
115	−44.0	−4451.2	−4580.7	9115.2	39.4	38.0
120	−58.2	−4636.4	−4776.6	9524.1	53.0	50.0
125	−77.5	−4870.9	−5016.8	10,036.8	71.7	66.5
130	−101.7	−5161.7	−5307.9	10,666.7	95.3	87.3
135	−130.6	−5517.2	−5657.9	11,429.2	123.5	112.1
140	−163.8	−5946.6	−6075.8	12,342.2	156.1	140.6
145	−200.8	−6461.2	−6872.1	13,426.8	192.6	172.4

The influence of the electron correlation on the angular strain was estimated by the SCS-MP2(fc)/cc-pVTZ method at the HF/cc-pVTZ geometries. The difference in the SCS-MP2 energies $\Delta E(MP2)$ is given in the last column. The HCH angle θ is parametrically varied from 106.5° (the equilibrium cyclohexane value) to 145°. The CCC angle is constant being 120° due to D_{6h} symmetry.

Let us now consider the almost strain free cyclohexane **4** (Fig. 2). Obviously, if the heavy carbon atoms are forced to lie in the same plane, then a large angular strain should occur, since all CCC angles are 120° by symmetry. Hohlneicher and Packschies[10] used homodesmotic[20] Eq. 1 for planar **4**$_{pl}$ cyclohexane (Fig. 2) and found irregular behavior of the V_{ne} term. There is, however, little sense in using Eq. 1 for artificially deformed structures. Homodesmotic reactions seem to be an unavoidable approach inspite of their imperfections for the stable strained structures. However, if the equilibrium geometries (absolute minima on the PES) are arbitrarily distorted, then the distortion energies are conveniently 'measured' against the ground state energy obtained at the optimized structure. This is exactly what we did here for planarized cyclohexane possessing D_{6h} symmetry:

$$E_s(\mathbf{4}) = E_{HF}(\text{cyclohexane})_{D_{6h}} - E_{HF}(\text{cyclohexane})_{opt} \qquad (4)$$

Results of the HF/cc-pVTZ energy decomposition analysis are presented in Table 3. It is evident that the angular strain and the V_{ne} values increase with the increase in the bond bending taking place in the carbon atom framework and in the CH bonds. A decreased Coulomb attraction leads to increased CC bond distances in planar cyclohexane and to a diminished V_{nn} term. This chain of causes and consequences was reversed by Hohlneicher and Packschies.[10] We find it more appropriate to consider the stabilization interactions first, since they in *ultima linea* lead to stable structures. The correlation energy contributions are easily deduced from Table 3. They are negative being in the absolute values smaller than 10% of the ΔE(HF) energies for lower θ, and slightly higher than 10% for very strong deformations (large θ angles). The optimized CC and CH bond distances and NBO hybridization parameters are given in Table S3 of Supplementary data.

To summarize, the present results show convincingly that the angular strain is considerably affected by unfavourable nucleus–electron attraction. It should be strongly pointed out that the magnitude and influence of the V_{ne} term could be overshadowed by other features, for example, the aromatic character of the CC bent bonds in the cyclopropane ring[21–23] and their antiaromatic behavior in the cyclobutane ring.[24] Therefore, each system exhibiting distorted structures and deformed electron density distributions should be examined very carefully, since they possess most likely a number of unusual features. The increased nucleus–electron attraction is expected to affect significantly the energetic features of strained systems in most cases, whereas the anomalous behavior of the V_{ne} term should be useful in some situations for diagnostic purposes. As to the unbalanced interactions embodied in the common homodesmotic reactions (1), which is an interesting problem per se, they will be discussed in more detail elsewhere.

Acknowledgements

Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2007.12.036.

References and notes

1. Barić, D.; Maksić, Z. B. *Theor. Chem. Acc.* **2005**, *114*, 222.
2. George, P.; Trachtman, M.; Bock, C. W.; Brett, A. M. *Tetrahedron* **1976**, *32*, 317.
3. Franklin, J. L. *Ind. Eng. Chem.* **1949**, *41*, 1070.
4. Cohen, N.; Benson, S. W. *Chem. Rev.* **1993**, *93*, 2419.
5. Coulson, C. A.; Moffitt, W. E. *Philos. Mag.* **1949**, *40*, 1.
6. Randić, M.; Maksić, Z. B. *Theor. Chim. Acta* **1965**, *3*, 59.
7. Klasinc, L.; Maksić, Z. B.; Randić, M. *J. Chem. Soc. A* **1966**, 755.
8. Maksić, Z. B.; Kovačević, K.; Eckert-Maksić, M. *Tetrahedron Lett.* **1975**, 101.
9. A more sophisticated method is given by the properties of the charge density at bond critical points. See, for example, Grimme, S. *J. Am. Chem. Soc.* **1996**, *118*, 1529.
10. Hohlneicher, G.; Packschies, L. *Tetrahedron Lett.* **2007**, *48*, 6429.
11. Moeller, C.; Plesset, M. S. *Phys. Rev.* **1934**, *46*, 618.
12. Dunning, T. H., Jr. *J. Chem. Phys.* **1993**, *98*, 7059.
13. Grimme, S. *J. Chem. Phys.* **2003**, *118*, 9095.
14. Wiberg, K. B.; Murcko, M. A. *J. Mol. Struct. THEOCHEM* **1988**, *169*, 335. and references cited therein.
15. Foster, J. P.; Weinhold, F. *J. Am. Chem. Soc.* **1980**, *102*, 7211; . *J. Chem. Phys.* **1983**, *78*, 4066.
16. Randić, M.; Maksić, Z. B. *Chem. Rev.* **1972**, *72*, 43.
17. Maksić, Z. B. *Comput. Maths Appl.* **1986**, *12B*, 697.
18. Maksić, Z. B.; Eckert-Maksić, M.; Rupnik, K. *Croat. Chem. Acta* **1984**, *57*, 1295.
19. Testa, B. *Principles of Organic Stereochemistry*; Marcel Dekker: New York, 1979.
20. A better term would be quasi-homodesmotic, see Ref. 1.
21. Dewar, M. J. S. *J. Am. Chem. Soc.* **1984**, *106*, 669.
22. Cremer, D.; Kraka, E. *J. Am. Chem. Soc.* **1985**, *107*, 3800.
23. Cremer, D.; Gauss, J. *J. Am. Chem. Soc.* **1986**, *108*, 7467.
24. Moran, D.; Manoharan, M.; Heine, T.; Schleyer, P.; von, R. *Org. Lett.* **2003**, *5*, 23.