Tetrahedron Letters 51 (2010) 2920–2923

Contents lists available at ScienceDirect

Tetrahedron Letters

journal homepage: www.elsevier.com/locate/tetlet

Strain in [*n*]triangulanes

Igor Novak

Faculty of Science, Charles Sturt University, PO Box 883, Orange NSW 2800, Australia

ARTICLE INFO

Article history:
Received 29 September 2009
Revised 15 March 2010
Accepted 26 March 2010
Available online 31 March 2010

Keywords:
Triangulanes
Strain energy

ABSTRACT

The molecular structures and strain energies of some [*n*]triangulanes have been studied by high-level ab initio calculations and compared with results for [*n*]ladderanes. The calculations provided several unexpected results. We show that the strain energies in triangulanes are smaller than previously suggested. The estimated strain energies in individual rings reveal that those with a larger number of proximal C–C bonds (inner rings) are more strained than peripheral rings with distal bonds. The total electron energies of branched and isomeric unbranched triangulanes are virtually identical. The strain energies of cyclotriangulanes are much smaller than previously estimated which makes them more easily achievable synthetic targets than earlier thought.

Triangulanes (oligospirocyclopropane systems) are an interesting class of compounds for several reasons. They are highly strained molecules as expected in view of the fact that they are composed of strained cyclopropane rings. Yet many of them exhibit surprising thermal stability.[1] Triangulanes exhibit numerous possible stereoisomers and show very large specific optical rotations. ^{13}C NMR spectra of triangulanes reveal the presence of three types of carbon atoms. The first type has small chemical shifts and corresponds to CH_2 groups of terminal three-membered rings. The second group has larger chemical shifts and corresponds to internal rings while the last group of carbon atoms is most shielded and corresponds to spiroatoms. Similarly, studies on the molecular structure of triangulanes using X-ray or electron diffraction have revealed the presence of four different types of CC bonds in triangulanes. The distal bonds are the longest (1.524 Å) while proximal–proximal bonds are the shortest (1.454 Å).

The properties of triangulanes have been reviewed recently in detail.[1] However, most triangulanes have not been studied by high level computational methods, but were studied by low level methods such as molecular mechanics and semiempirical or Hartree–Fock methods. Since strain energy (SE) is one of the core properties of triangulanes it needs to be reassessed using high level computational methods. This is the purpose of this work.

The quantum chemical calculations were performed using the GAUSSIAN 03 program.[2] The total electronic energy for each molecule was computed using the G3MP2/B3LYP method[3] which has root-mean-square deviation in energy of approximately 4 kJ/mol. The method includes full geometry optimization at the B3LYP/6-31G* level followed by single point QCISD (quadratic configuration interaction single and double) type calculations. All the optimized structures corresponded to minima on their potential energy surfaces as was inferred from the absence of negative values of vibrational force constants. The B3LYP/6-31G* geometries (bond lengths, angles) were in good agreement with the molecular structures of triangulanes determined by X-ray diffraction.[1] The agreement between the calculated and measured bond lengths and angles was within 0.01 Å and 1°, respectively.

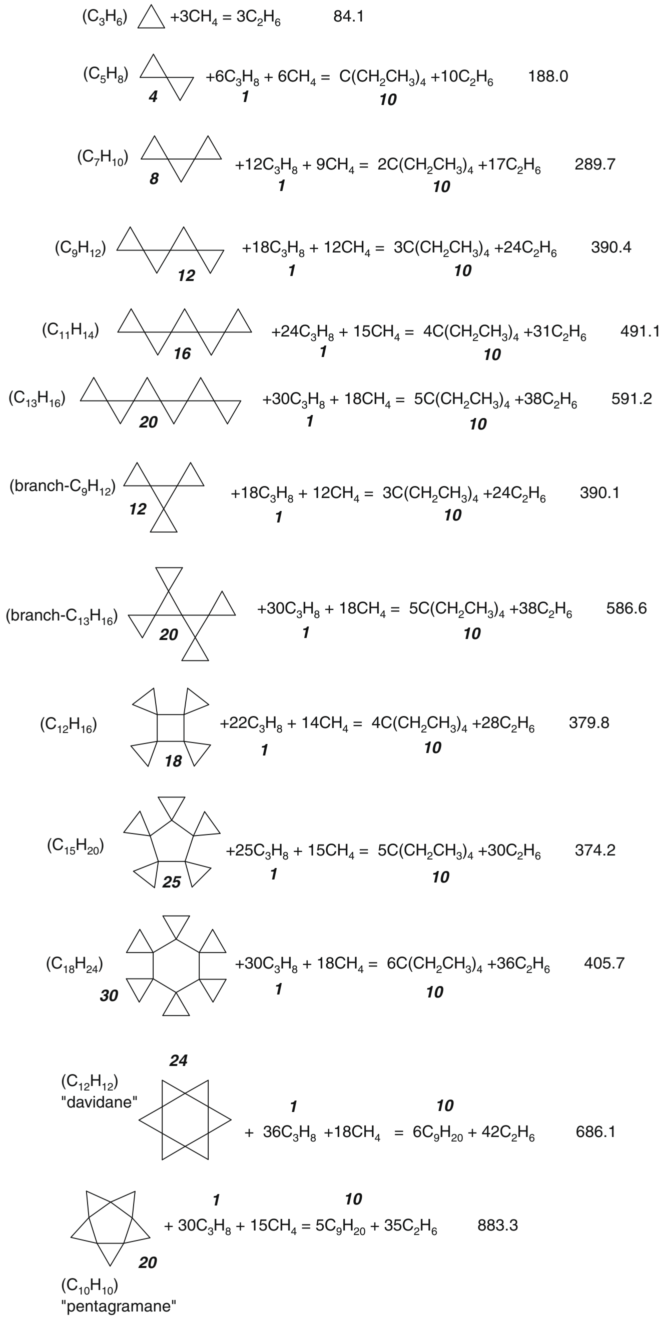
Calculation of the strain energies (SE) can be achieved using high-level computational methods and isodesmic reaction schemes. The sign convention for SE in this work is defined as the negative value of enthalpy of the corresponding isodesmic reaction. There are several ways in which such reaction schemes can be set up for any particular problem, i.e. the schemes are not unique. However, it has been shown that group equivalent schemes work best,[4] and these were used in this work. Such schemes preserve the number and type of functional groups present on going from reactants to products. There is another important consideration which needs to be taken into account when studying strain energies in alkanes. The presence of 1,3-carbon–carbon non-bonding interactions (protobranching) has been debated for a long time and is the subject of some controversy. Some researchers claim that these interactions are stabilizing while others report that they are destabilizing.[5] We have set up isodesmic reactions in Schemes 1 and 3 so that the total number of 1,3-interactions is equal in the reactant and product molecules, and the interactions are thus approximately compensated in each reaction scheme. As mentioned above, there are several ways in which hypothetical reactions can be set up so as to keep the number of C–C and C–H bonds equal in the reactants and products. Simpler reaction schemes can be set up for each of the reactions listed in Scheme 1. These simpler reactions are given in Scheme 2.

However, in the simpler reactions (Scheme 2), 1,3-interactions are not cancelled as can be seen from the number of 1,3-interac-

---

E-mail address: inovak@csu.edu.au

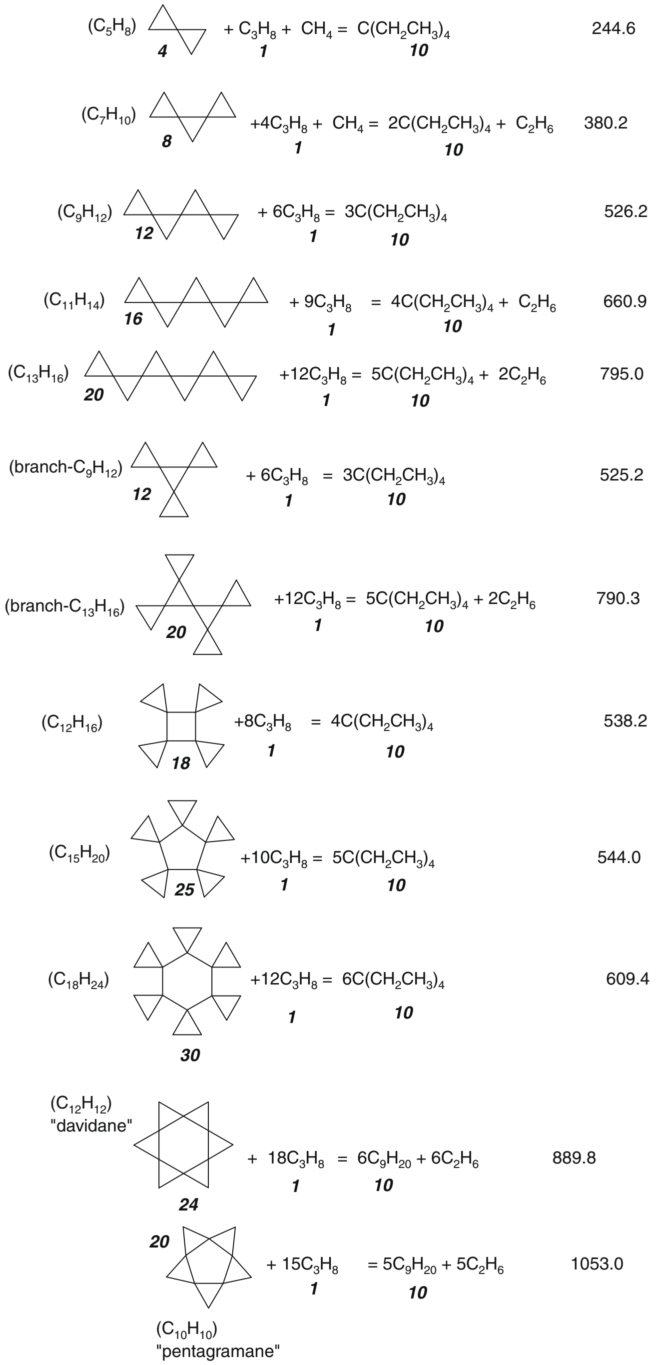
0040-4039/$ - see front matter © 2010 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tetlet.2 010.03.108



Scheme 1. Isodesmic reactions used to calculate total SE (kJ/mol) of triangulanes which compensate for 1,3-interactions. The molecular formulae are given in brackets. The rightmost numbers are absolute values of enthalpies of the isodesmic equations and correspond to the total SE of the respective triangulanes. The number of 1,3-interactions present in individual molecules are given by numbers in bold italic.

tions present in individual molecules. The SE values calculated via Schemes 1 and 2 differ by more than 50 kJ/mol. This demonstrates that complex reaction schemes which carefully balance 1,3-interactions are necessary to obtain representative SE values.

Inspection of the results presented in Scheme 1 and Table 1 shows that the total strain energies in triangulanes increase with the number of three-membered rings, as expected. The strain energy per carbon atom also increases and is higher in the triangulanes described here than in ladderanes, another class of strained hydrocarbons (Fig. 1) that we described earlier.[6] This is expected since ladderanes contain less-strained four-membered rings compared to the three-membered rings present in triangulanes.



Scheme 2. Simple isodesmic reactions which can be used to calculate the total SE (kJ/mol) for triangulanes but which neglect 1,3-interactions. The molecular formulae are given in brackets, the rightmost numerical values correspond to the total SE, while bold italic numbers indicate the number of 1,3-interactions present in specific molecules.

Our values for strain energy are smaller than those previously reported (Table 1) which may be due to higher level of theory employed in our calculations and due to compensation of 1,3-interactions achieved in our reaction schemes. The smaller strain energy values obtained in this work are also consistent with the considerable thermal stability of the triangulanes.[1] Another interesting result concerns the C_9H_{12} isomers which have almost identical total energies (Table 1). One must bear in mind that one of the C_9H_{12} isomers is a branched triangulane while the other one is an unbranched triangulane. This suggests that the topology of the trian-

Table 1
Total strain energies (SE), total energies (E) and strain energies per carbon (SE/*n*) for triangulanes at the G3MP2/B3LYP level[a]

Molecule (Scheme 1)	SE (kJ/mol)	*E* (a.u.)	SE/*n* (kJ/mol)	SE/*n* (kJ/mol) ladderanes
C_3H_6	84.1 (117.7)	−117.659365	28.0	
[1]-ladder				22.3
C_5H_8	188.0 (272)	−194.897968	37.6	
C_6 [2]-ladder				29.6
C_7H_{10}	289.7 (412.2)	−272.137432	41.4	
C_8 [3]-ladder				32.8
C_9H_{12}	390.4 (578.4)	−349.377250	43.4	
C_{10} [4]-ladder				33.5
$C_{11}H_{14}$	491.0 (698.5)	−426.617092	44.6	
C_{12} [5]-ladder				35.0
(branch) C_9H_{12}	390.1 (575.7)	−349.377654	43.3	
$C_{13}H_{16}$ (branch)	586.6	−503.858890	45.1	
$C_{13}H_{16}$ (unbranched)	591.2	−503.857128	45.5	
C_{14} [6]-ladder				35.1
$C_{12}H_{16}$	379.8	−465.898689	31.6	
$C_{15}H_{20}$	374.2	−582.422262	25.0	
C_{16} [7]-ladder				36.0
$C_{18}H_{24}$	405.7	−698.923240	22.5	
C_{18} [8]-ladder				36.9
$C_{10}H_{10}$	883.3	−386.054470	88.3	
$C_{12}H_{12}$	686.1	−463.407738	51.2	

SE/*n* values for ladderanes are also shown for comparison.

[a] Values in brackets are taken from Refs. 1 and 7.

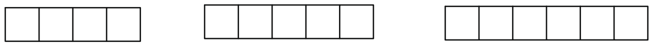
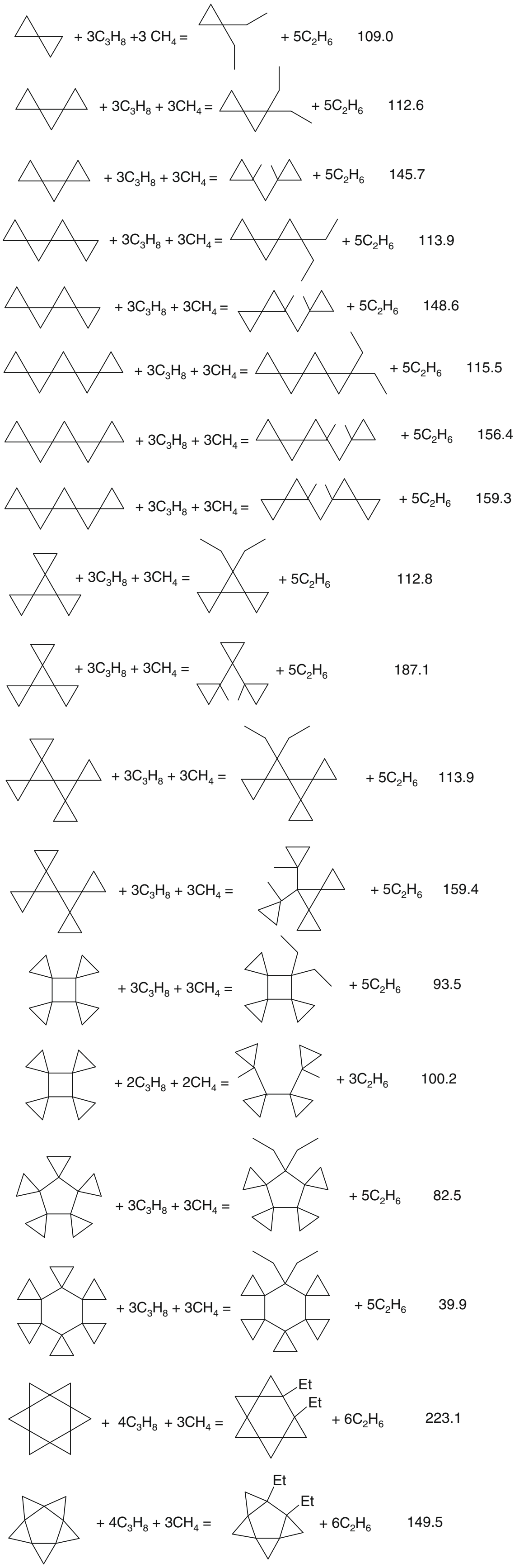


Figure 1. Structures of [4]-, [5]- and [6]-ladderanes.

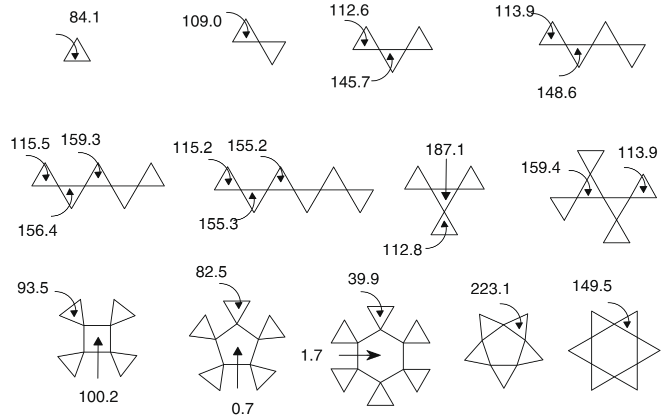
gulane molecule is not significant in determining its thermodynamic stability, but depends on the number of three-membered rings present. This comment does not apply to cyclotriangulanes which contain rings other than cyclopropane. Cyclotriangulanes have SE values which are very different from other triangulanes.

We have also estimated the strain of individual rings in triangulanes (Scheme 4). The results indicate that the ring strain in peripheral rings is smaller than in the internal rings. This observation is consistent with experimental data on the structures of these molecules. As mentioned previously, the distal C–C bonds (which are constituent parts of external rings) are longer than the proximal bonds which are involved in forming internal three-membered rings. Another interesting observation is that in cyclotriangulanes the approximate additivity of SE for individual rings breaks down. For example, in pentagramane the SE of the cyclopropane rings are considerably higher than in cyclopropane itself. This can explain why the previous estimates, which were based on the assumption of SE ring additivity,[7,8] gave much lower values for total SE.

In summary, we have studied the strain energy in triangulanes and arrived at several unexpected conclusions. The strain energies of the title molecules are smaller than previously suggested which is consistent with considerable thermal stability of non-cyclic triangulanes. The external rings in triangulanes are less strained than the internal rings which is the opposite of the individual ring strain energies calculated for ladderanes. This suggests that in the chemical reactions of triangulanes which involve ring-opening or rearrangements, the internal rings are likely to be involved in the initial reactions steps. This is again different from ladderanes where the terminal rings are likely to rupture first leading to a 'zipper' mechanism.[6] We found that the total (and per carbon atom) ring strain in cyclotriangulanes is much smaller than previously estimated,[1,7,8] and conclude on the basis of our results, that they represent more achievable synthetic targets than earlier thought.



Scheme 3. Isodesmic reactions used to calculate the SE (kJ/mol) of individual rings.



Scheme 4. SE (kJ/mol) for individual rings calculated using the isodesmic reactions from Scheme 3.

Acknowledgement

I.N. thanks the Faculty of Science, Charles Sturt University for financial support of this work through the Seed Grant A105-954-639-3495.

References and notes

1. (a) de Meijere, A.; Kozhushkov, S. I.; Schill, H. *Chem. Rev.* **2006**, *106*, 4926; (b) de Meijere, A.; Kozhushkov, S. I. *Chem. Rev.* **2000**, *100*, 93. and references cited therein.
2. Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J.M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Gonzalez, C.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A., GAUSSIAN 03, Revision E1, Gaussian: Pittsburgh PA, 2003.
3. Baboul, A. G.; Curtiss, L. A.; Redfern, P. C.; Raghvachari, K. *J. Chem. Phys.* **1999**, *110*, 7650.
4. Bachrach, S. *Computational Organic Chemistry*; Wiley-Interscience: New York, 2007.
5. (a) Wodrich, M. D.; Wannere, C. S.; Mo, Y.; Jarowski, P. D.; Houk, K. N.; von Schleyer, P. R. *Chem. Eur. J.* **2007**, *13*, 7731; (b) Gronert, S. *Chem. Eur. J.* **2009**, *15*, 5382.
6. Novak, I. *J. Phys. Chem. A* **2008**, *112*, 10059.
7. Beckhaus, H.-D.; Ruchardt, C.; Kozhushkov, S. I.; Belov, V. N.; Verevkin, S. P.; de Meijere, A. *J. Am. Chem. Soc.* **1995**, *117*, 11854.
8. Ball, D. W. *J. Phys. Org. Chem.* **2008**, *21*, 387.