Tetrahedron Letters 57 (2016) 5616–5619

Contents lists available at ScienceDirect

Tetrahedron Letters

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

Kinetic energy density per electron as quick insight into ring strain energies

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ARTICLE INFO

Article history:
Received 9 October 2016
Revised 27 October 2016
Accepted 31 October 2016
Available online 2 November 2016

Keywords:
Ring strain
Atoms in molecules
Kinetic energy density
Cyclopropanes
Cyclobutanes
Three-membered heterocycles

ABSTRACT

An easy and computationally inexpensive way of estimating ring strain energies (RSE) is presented. It is based on the AIM-derived kinetic energy density per electron quantity, $G(\mathrm{r})/\rho(\mathrm{r})$, computed at the ring critical point, which in general exhibits better linear correlation towards RSE than the previously reported method based on $G(\mathrm{r})$ itself.

Introduction

Ring strain is the most characteristic property of small cyclic systems[1] whose internal bond angles are remarkably compressed in relation to idealized (non-strained) values[2]. It results from a combination of angle (Baeyer),[3] torsional (eclipsing or Pitzer) and transannular (van der Waals) strains. The resulting excess of internal energy is liberated in combustion reactions.[4] The high spring-loaded energy and exceptional bonding situation in ring strained molecules can be employed to drive reactions in a synthetically useful manner, such in ring opening reactions (ROR) and polymerisations (ROP). Therefore calculation of ring strain energies (RSE) has become a topic of paramount importance[5] and large efforts have been devoted to the estimation of RSE in both organic[3,6] and inorganic[7] small ring systems. Evaluation of RSE requires setting up appropriate balanced chemical reactions where the reactant is the strained molecule and the products are unstrained reference species, so that all effects are compensated at both sides of the equation excepting ring strain itself. On the basis of mainly bonding, number of electron pairs and hybridization criteria[8] the aforementioned balanced equations can be classified in several categories, such as isodesmic,[9] homodesmotic,[8,10] hyperhomodesmotic,[11] etc.

Bader's theory of atoms-in-molecules (AIM)[12] has been also introduced for studying ring strain, as originally shown in the pioneer work of Bachrach in phosphirane and phosphetane rings.[13] Later on Grimme established a relationship between ring strain and properties of the electron density at bond critical points (BCP), but requiring a comparison with values in strainless reference compounds to predict bond and total strain energies.[14] More recently Frontera reported an easy way of estimating RSE by virtue of an almost linear correlation with the kinetic energy density $G(\mathrm{r})$ computed at the ring critical points (RCP).[15] The procedure was checked for three different series, with good linear correlations: 1) equally substituted three- to six-membered cycloalkanes (unsubstituted, methylsubstituted and 1,1-dimethylsubstituted), 2) a wide range of three-membered carbocycles (cyclopropanes and cyclopropenes) and 3) methylene- and insaturated three- to six-membered rings (methylencycloalkanes, cycloalkenes and cycloalkanones). Also a moderate linear correlation was found for an small set of three-membered heterocycles (oxirane, aziridine, thiirane and phosphirane). This approach has been successfully used to assess ring strain in three[16] and four-membered[17] phosphorus heterocycles.

Herein better linear correlations, in most cases (similar in the others), between RSE and the kinetic energy density per electron, $G(\mathrm{r})/\rho(\mathrm{r})$, are presented.

Results and discussion

For this study, the same set of three- and four-membered carbocycles of Frontera's work[15] were selected (Figure 1) and their RSE values retrieved from that report.

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http://dx.doi.org/10.1016/j.tetlet.2016.10.115

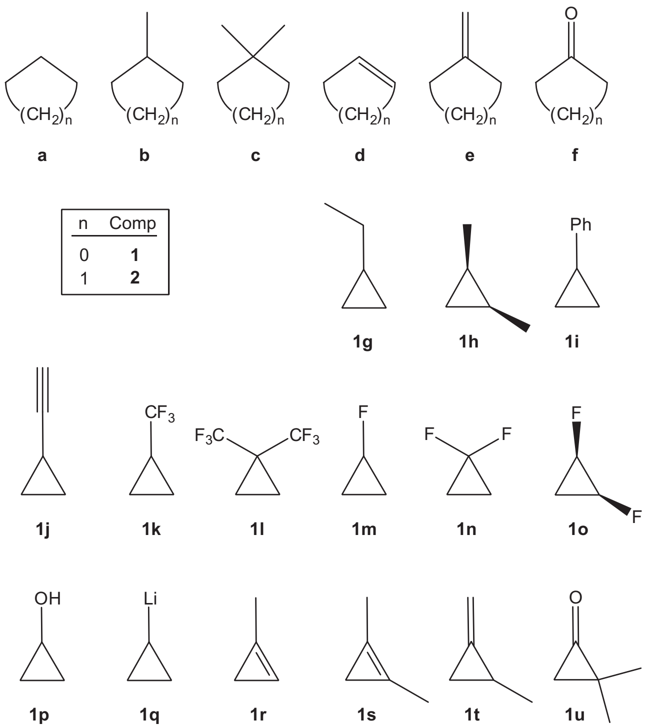


Figure 1. Carbocyclic species studied.

Furthermore, two series of oxiranes (**3**) and aziridines (**4**) have been included in the present study (Figure 2). Their substitution pattern was chosen so as to cover a wide range of ring strain.

Only the heterocyclic parent compounds were included in Frontera's study and additional computed RSE values are available for either oxirane (**3a**)[18] and aziridine (**4a**).[19] The RSE for all other heterocyclic compounds **3** and **4** were computed in the present work, including oxiranone (**3e**) and aziridinone (**4e**) whose reported values[20] turned out to be too high when plotted together with other derivatives (*vide infra*). The RSE were obtained by means of three homodesmotic reactions, one for the cleavage of every endocyclic bond (Scheme 1), and averaging the three zero-point energy corrected values computed at the DLPNO-CCSD(T) level (see Computational Details). Conformations of final products of C2-E and C3-E cleavage showing E–H···E hydrogen bonds were discarded.

All structures were optimized at the working DFT level of theory and the corresponding AIM-derived properties recomputed at the respective RCPs (Table 1).

According to the regression coefficients, graphical representation of RSE versus the kinetic energy density $G(r)$ shows moderate linear dependency for cyclopropane (**1**) and cyclobutane (**2**) derivatives whereas only the aziridine (**4**) series exhibits a remarkably good correlation (Figure 3a). It is worth mentioning that the oxirane (**3**) series does not correlate at all, although it could be interpreted as a moderate correlation if the point corresponding to oxiranone is removed. Very interestingly, the plot of RSE versus the kinetic energy density *per electron*, $G(r)/\rho(r)$, displays much better linear correlations for the cyclopropane (**1**), oxirane (**3**) and aziridine (**4**) series, whereas the cyclobutane (**2**) series shows linear correlation of almost the same quality.

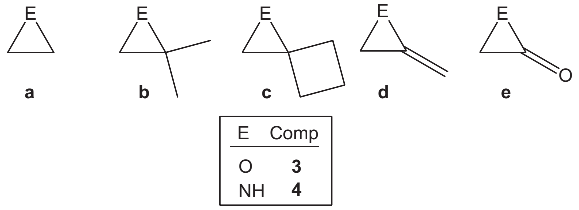
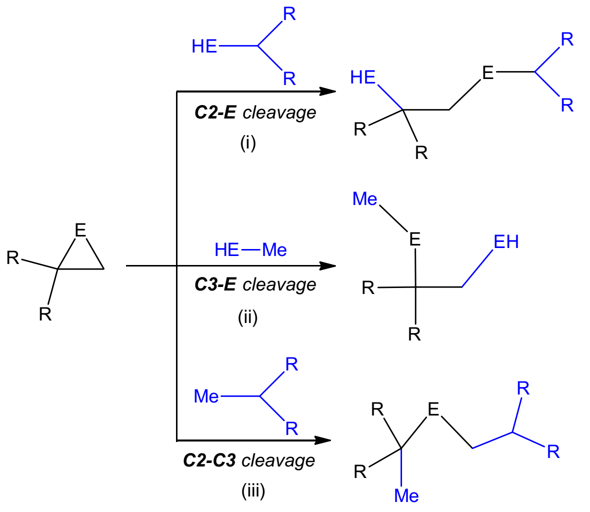


Figure 2. Oxiranes (E=O) and aziridines (E=NH) studied.



Scheme 1. Homodesmotic reactions used for evaluation of RSE.

Table 1
RSE (kcal/mol) and AIM-derived parameters (au) at RCP for compounds **1–4**.

	RSE	G(r)	ρ(r)	G(r)/ρ(r)
1a	29.0[a]	0.1473	0.1996	0.7383
1b	27.6[a]	0.1482	0.1993	0.7437
1c	27.2[a]	0.1472	0.1987	0.7411
1d	54.5[a]	0.1844	0.2164	0.8520
1e	38.8[a]	0.1597	0.2019	0.7913
1f	45.1[a]	0.1596	0.1920	0.8317
1g	26.5[a]	0.1484	0.1995	0.7436
1h	30.8[a]	0.1485	0.1978	0.7505
1i	26.5[a]	0.1480	0.1992	0.7429
1j	29.1[a]	0.1448	0.1974	0.7337
1k	28.1[a]	0.1490	0.2004	0.7437
1l	26.4[a]	0.1489	0.1998	0.7452
1m	33.3[a]	0.1549	0.2024	0.7650
1n	39.5[a]	0.1571	0.1998	0.7863
1o	39.5[a]	0.1622	0.2029	0.7991
1p	32.1[a]	0.1530	0.1988	0.7696
1q	22.2[a]	0.1399	0.1921	0.7282
1r	54.5[a]	0.1856	0.2161	0.8589
1s	51.5[a]	0.1871	0.2158	0.8668
1t	38.0[a]	0.1611	0.2018	0.7984
1u	46.1[a]	0.1620	0.1911	0.8476
2a	26.2[a]	0.0986	0.0861	1.1449
2b	25.7[a]	0.0988	0.0863	1.1453
2c	23.7[a]	0.0970	0.0851	1.1408
2d	30.6[a]	0.1212	0.0954	1.2700
2e	26.9[a]	0.1027	0.0865	1.1874
2f	28.7[a]	0.1140	0.0899	1.2674
3a	25.7[a,b]	0.2066	0.2160	0.9567
3b	24.3	0.2063	0.2134	0.9671
3c	27.2	0.2112	0.2167	0.9748
3d	35.1	0.2216	0.2184	1.0149
3e	40.3[c]	0.2069	0.2054	1.0075
4a	27.0[a,d]	0.1789	0.2093	0.8548
4b	24.9	0.1791	0.2079	0.8615
4c	29.0	0.1835	0.2109	0.8700
4d	40.3	0.1988	0.2156	0.9225
4e	50.0[c]	0.2030	0.2080	0.9762

[a] Reported in Ref. 15.
[b] Reported as 26.4 kcal/mol in Ref. 18.
[c] Reported in Ref. 20 as 47.0 (**3e**) and 55.0 (**4e**) kcal/mol.
[d] Reported as 27.6 kcal/mol in Ref. 19.