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On the Relative Stability of Cycloalkanes

Bernd M. Rode

Institut für Anorganische und Analytische Chemie,
Universität Innsbruck, A-6020 Innsbruck, Austria

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The relative stability of the cycloalkanes $n = 3$ to 8 is investigated by means of semiempirical (CNDO) and *ab initio* MO SCF calculations. It is found that the compensation of increasing nuclear repulsion by the gain of electronic energy reaches a maximum at $n = 6$, leading thus to a maximum of stability for $n = 6$, and that the usual qualitative models of hybridisation state, optimal bond angle and optimal hydrogen positions do not present sufficient explanations. The methods used, their limitations and basis set effects are discussed.

(Keywords: CNDO; Cycloalkanes; MO-SCF-calculations; Stability)

Relative Stabilitäten von Cycloalkanen

Die relativen Stabilitäten von Cycloalkanen ($n = 3$ bis 8) wurden mittels semiempirischer (CNDO) und *ab initio* MO SCF Berechnungen untersucht. Es wurde festgestellt, daß die Kompensation der steigenden Kernabstoßung durch Gewinn an elektronischer Energie bei $n = 6$ zu einem Maximum an Stabilität führt und daß das übliche qualitative Modell von Hybridisierungszuständen nicht zur Erklärung ausreichend ist. Die angewendeten Methoden, deren Grenzen und der Einfluß der gewählten Basissätze werden diskutiert.

Introduction

The relative stability of saturated cyclic hydrocarbons is an experimentally and theoretically well studied subject. The maximum of stability of the six-membered ring and its importance in relation to the other compounds is even reflected by the number of papers refered to in "Chemical Abstracts" from 1972-1980:

Cyclopropane: 2567, cyclobutane: 974, cyclopentane: 1174, cyclohexane: 6629, cycloheptane: 487, cyclooctane: 574.

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Several qualitative theoretical explanations have been given so far, why the six-membered ring should be the most stable one. These approaches rank from geometrical considerations like favourisation of the tetrahedral angle or steric effects (possibility of staggered hydrogen positions, *Pitzer* tension a.s.o.) to models concerning the electronic structure as hybridisation at the carbon atom.

Quantitative molecular orbital studies for this series of compounds by means of *ab initio* or at least semiempirical SCF procedures have been performed, however, only for cyclopropane and cyclobutane[1–4]. It seemed to be of interest, therefore to perform a complete series of both *ab initio* and semiempirical MO SCF calculations for the ring compounds from $n = 3$ to $n = 8$ in order to see, whether the usual qualitative explanations are justified and sufficient to describe the phenomenon "ring stability".

Method

Semiempirical calculations have been performed by means of the standard CNDO/2 method[5, 6] in its original parametrization. The all electron *ab initio* calculations used a minimal GLO basis set (exponents in Ref.[7]) and a 8 s/4 p *Huzinaga* basis set[8].

All molecules were calculated at their experimental or at their energy optimized calculated geometry[9–13].

The calculations have been performed partly at the computer center of the University of Innsbruck, partly at the interuniversitary computer center at the Technical University of Vienna.

Results and Discussion

In order to investigate the main factors contributing to the stabilization of cycloalkanes it seemed to be useful to evaluate total energies, electronic energies and repulsion forces between the nuclei per CH_2 unit throughout the series. Within the semiempirical method we calculated *Wiberg* bond indices[14] for the C—C bond and the relative contributions of s and p functions. The latter values might be compared with model assumptions based on a "hybridization state" of carbon (although such considerations seem to have little meaning within the framework of exact quantum chemistry). These values were obtained by summation of percentual contributions of carbon s and p functions over all occupied eigenvectors and normalizing the total contributions to the value of 1 for the s contribution.

In Table 1, energy values, bond indices and sp contributions calculated by the CNDO/2 method are collected. Table 2 summarizes

Table 1. *Calculated CNDO/2 energy values in atomic energy units per methylene group for cycloalkanes ($n = 3$ to 8), Wiberg bond indices for* C—C *bonds and s/p relation in binding carbon functions*

n	3	4	5	6	7	8
E electronic	−22.986	−26.460	−29.692	−32.686	−35.302	−37.790
E nucl. rep.	14.329	17.777	20.988	23.978	26.592	29.087
E total	−8.657	−8.683	−8.703	−8.709	−8.710	−8.704
Bond Index	0.985	0.999	1.020	1.015	1.023	1.015
s/p relation	1:3.14	1:3.02	1:3.02	1:3.03	1:3.02	1:3.02

Table 2. *Ab initio energy values obtained by the minimal* (a) *and* 8 s 4 p (b) *basis set in atomic energy units per methylene group*

n	3	4	5	6	7	8
E electr. (a)	−58.271	−64.623	−70.467	−75.876	−80.579	−84.929
E electr. (b)	−64.176	−70.480	−76.333	—	—	—
E nucl. rep.	25.176	31.476	37.320	42.720	47.430	51.782
E H/H rep.	4.2E-04	5.5E-04	6.7E-04	7.9E-04	9.0E-04	1.0E-03
E total (a)	−33.096	−33.148	−33,147	−33.157	−33.149	−33.147
E total (b)	−39.000	−39.004	−39.013	—	—	—

the corresponding energy values obtained by *ab initio* calculations, supplemented by an additional calculation of the H atom repulsions in the molecules.

Semiempirical Calculations

The values for the total energy indicate a maximum of stability for a ring size of 5 to 7. The differences between these three rings are too small to be significant. One fact seems to turn out quite clearly, namely, that the six membered ring does not represent a maximum in electronic stabilization or any "optimal binding situation", since the electronic energy increases strongly also upon further enlargement of the ring. The evaluation of s and p contribution to the binding state of carbon also confirms little importance of the angle for the actual representation of these functions in the total wave function. The *Wiberg* indices are also very similar within the series, except for the smallest rings, where they are smaller than 1, which is the typical value for a single bond. Both "hybridisation state" and bond index support the generally accepted postulate of nonlinear ("banana") bonds in cyclopropane. The rather small energy differences between the 5, 6 and 7-ring indicate the semiempirical method to be not sufficient for a reliable answer concerning the optimal stability of cyclohexane. Full explicite consideration of all integrals and the inclusion of inner shell electrons seemed to be inevitable, therefore, for the further studies of this series.

Ab initio Calculations

For the discussion of the *ab initio* results we have separated the total energy values into electronic energy and nuclear repulsion forces, as they result from the HF SCF procedure based on the *Born-Oppenheimer* approximation. This energy separation proved to be useful already in other investigations concerning structure and stability of compounds[15–17] and allows an estimation of the influence of the molecular geometry on the mutual compensation of stabilizing binding forces and repulsive electrostatic forces in the molecule.

The results obtained by the small basis set show more distinct differences between the six-membered ring and the other compounds. The former ring is more stable by about 5 kcal/mole. The main reason for the maximum stabilization of the six-membered ring results from the difference between electronic energy and nuclear repulsion. The electronic contribution to ring stabilization increases by the insertion of a further methylene unit into the ring. At the same time, nuclear repulsion also increases, but both effects are not completely parallel. For cyclohexane, the compensation of the gain of electronic energy by nuclear repulsion is least precise. Therefore we have a net stabilization per methylene unit for the six-membered ring.

The values for the H/H repulsion have been calculated with the fractional charge of + 0.02 for the H atom, which is rather constant within the series. These data indicate, that the increase of hydrogen repulsion becomes smaller with increasing ring size. It does not seem very likely, therefore, that the geometrical arrangement of the H atoms in the cycloalkanes represents an important reason for a special stabilization of the six-membered ring.

The rather high stabilization value calculated by this method for cyclobutane indicates a basis set artefact. For small basis sets, mutual basis set improvements by functions of neighbouring atoms is a well known effect. Whereas in the case of our series this effect is constant for direct neighbours (and hence also not apparent in cyclopropane), it should occur mainly in the case of four membered ring, where the distance between diagonally opposite C atoms is only 1.403 times larger than the C—C bond distance. The calculations using the larger basis set prove this assumption to be correct, leading to a satisfactory series of stabilization values. For cyclopentane and larger rings, distances between nonneighbouring atoms become much larger so that this effect will be rather constant, since the functions used do not allow such an artificial basis improvement for the more distant atoms.

Another question arises from the overestimated destabilization energy for cyclopropane resulting from both semiempirical or minimal basis set *ab initio* calculations. Comparison with the value obtained by the larger basis set indicates, that the small number of basis functions is apparently not flexible enough to describe the special situation in this molecule satisfactorily. The high electron concentration thus leads to increased electron repulsion. The large basis set is much more suitable to account for bond deformation, which reduces electron repulsion.

Finally, electron correlation has not been considered so far in our work, although correlation energy differences can amount to several kilocalories per mole. Our calculations allow no conclusion on the influence of electron correlation on the results. It can be expected, that all stabilization energies will be lowered to some extent.

Since we are dealing with a series of homologues with almost identical binding conditions, one can surely expect the influence of correlation to be almost constant within the series and not to change the relative order. The only significant effect could be expected in the case of cyclopropane, where stabilization due to correlation effects might improve the *Hartree-Fock* value due to the location of all bonds within a rather restricted area. This point is surely worth further investigation but beyond the scope of this study. The rather satisfactory agreement between experimental data and the values obtained by the one determinantal approach based on larger basis set indicates, that the

Table 3. *Differences in heats of combustion per methylene group*[18] *and calculated stabilization energy differences. Values have been calculated relative to cyclopentane as the largest system treated by all methods. All values in kcal/mol per methylene group*

Method *n*	3	4	5	6	7	8
experimental	7.9	5.2	0	—1.3	—0.4	—0.1
ab initio 8 s/4 p basis	8.2	5.6	0	—	—	—
ab initio min. basis	33.4	—0.4	0	—5.9	—1.3	0.0
CNDO/2	28.8	12.5	0	—3.8	—4.4	—0.6

assumption of a negligible influence of correlation on the relative order is not far from being correct. This comparison will be given in the last part of this paper.

Theory and Experiment

We conclude the theoretical studies by a comparison to experimental data. The data which are most suitable for this purpose, are the heats of combustion of the cycloalkanes, relative to each other, since they reflect the energetic situation of the compound. Some uncertainty is contained in this comparison, since all calculated data necglect the differences in zero point energies. Nevertheless, the comparison given in Table 3 shows satisfactory agreement between the experimental data and the values obtained with the larger basis set.

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