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A 55 Rechnungen an Molekülen mit Kraftfeldern und quantenmechanischen Methoden

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Praktikum:

testiert am: 1/3/2017

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~~basics~~: objective:

With the help of force field methods, a structural optimization of the chair, twist and boat conformation of cyclohexan was carried out. Also the 1,2 Addition and the 1,4 Addition of hydrogen to Buckminster Fulleren C_{60} was investigated with force field method and EHT-method.

basics:

The force fied method.

The atoms are described as classical particles, ~~between~~ between which mechanical forces and electrostatic forces act. The electrons play no role. The ~~energy~~ force field energy can therefore be described as the amount of energies which result from atom interaction.

$E_{FF} = E_{cov} + E_{nb} = E_{str} + E_{bend} + E_{tors} + E_{vdw} + E_{el} + E_{cross}$

- E_{FF}: forcefield
- E_{cov}: covalent
- E_{nb}: non-covalent interaction
- E_{str}: stretch bond
- E_{bend}: angle bond
- E_{tors}: torsion
- E_{vdw}: van der Waals
- E_{el}: electrostatic
- E_{cross}: crossterm

If you now perform a geometry optimization and consider the deviations of bonding angles and length as well as the torsion angles, the potential energies of the conformations of cyclohexane can be compared. The lower the energy the better.

Extended Hückel theory

Since we consider a reaction in the second part of the experiment, we must also consider the electrons. So we use the more general semi-empirical extended Hückel theory, which also includes the π- and σ atom orbitals. The LCAO-approach (linear combination of atomic orbitals) is used. $\psi_i = \sum_{k=1}^{n} c_{ki} \chi_k$ χ_k: valence atom orbitals, c_{ki}: molecular orbitals coefficients

Source: description of experiment

discussion

part I : a) conformations of cyclohexan

The bond length of C-C doesn't change after optimization, the bond length of C-H is sligthly different but the changes of the angles are much larger. The minimization of the energy is the diving force here, especially the ring strain is minimized.

The driving force is mainly the steric hindrance of H atoms.

b) The boat conformation is optimized when the distance between H7 and H13 increases because of the Coulomb repulsion. The VanderWaals-Radius of one H is 1,2 Å [1] which means that the distance should be 2,4 Å between H7 and H13 so that the measured result (2,33 Å) has a accordance of 97% to the theoretical result

c) According to organical chemistry lectures the chair conformation is the most stable structure. As you can see in the diagrams the twist and boat conformation are energetically higher than the chair conformation which confirms experimentally the literature

part II :

b) As you can see in the last diagram attached, the force field method (MM+) is not useable for the geometrical optimization because it doesn't include the π- and σ-orbitals effects like the EHT. The DFT [2] is similar to EHT in the aspect of energy.

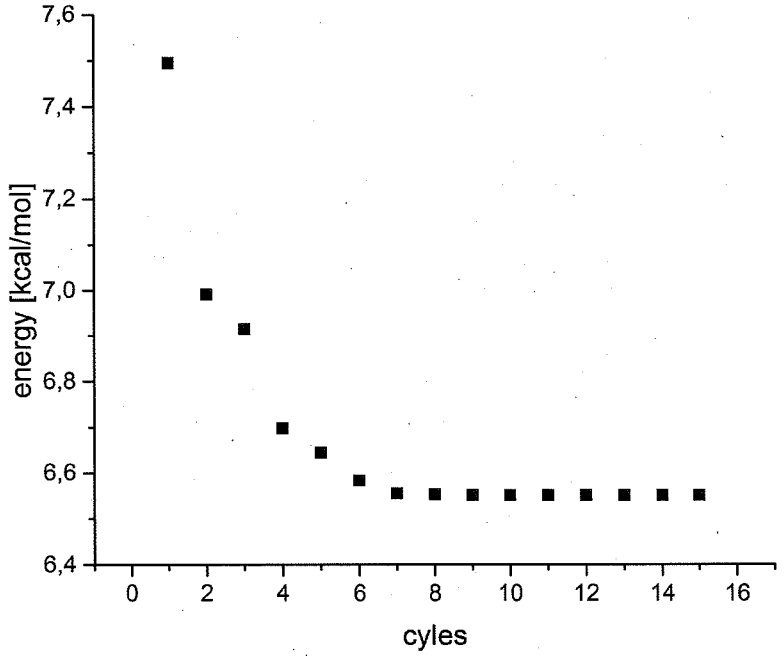
c) After adding two Hydrogens to the folleren, its structure is changed. While this chemical reaction the orbital configuration changes from sp^2 to sp^3 and because of this the EHT and DFT give similar results. The force field method doesn't consider the change in the orbitals and so the results are less accurate.

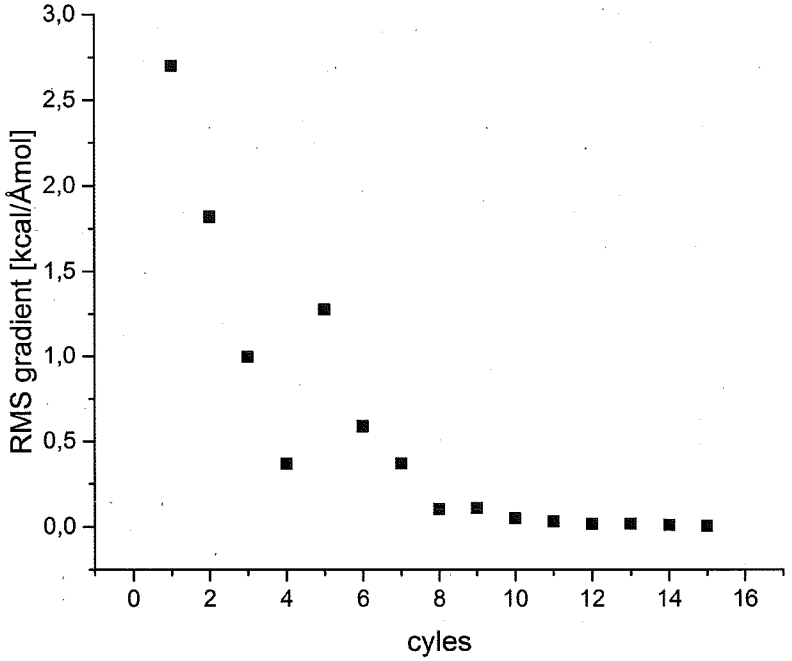
literature : - description of experiment
- (1) www.uniterra.de/rutherford/tab_waal.htm
- (2) Okamoto, Y. J. Phys. Chem. A 2001, 105, 7634-7637

Data analysis

Cyclohexan conformations

cyles	energy [kcal/mol]	RMS gradient [kcal/Åmol]
1	7,495117	2,701668
2	6,990516	1,820079
3	6,914451	0,996608
4	6,697163	0,369157
5	6,643705	1,276112
6	6,583475	0,587539
7	6,555391	0,370409
8	6,552749	0,103503
9	6,551652	0,109345
10	6,551139	0,050082
11	6,551072	0,031372
12	6,551012	0,016298
13	6,550988	0,017037
14	6,550978	0,01049
15	6,550974	0,003915



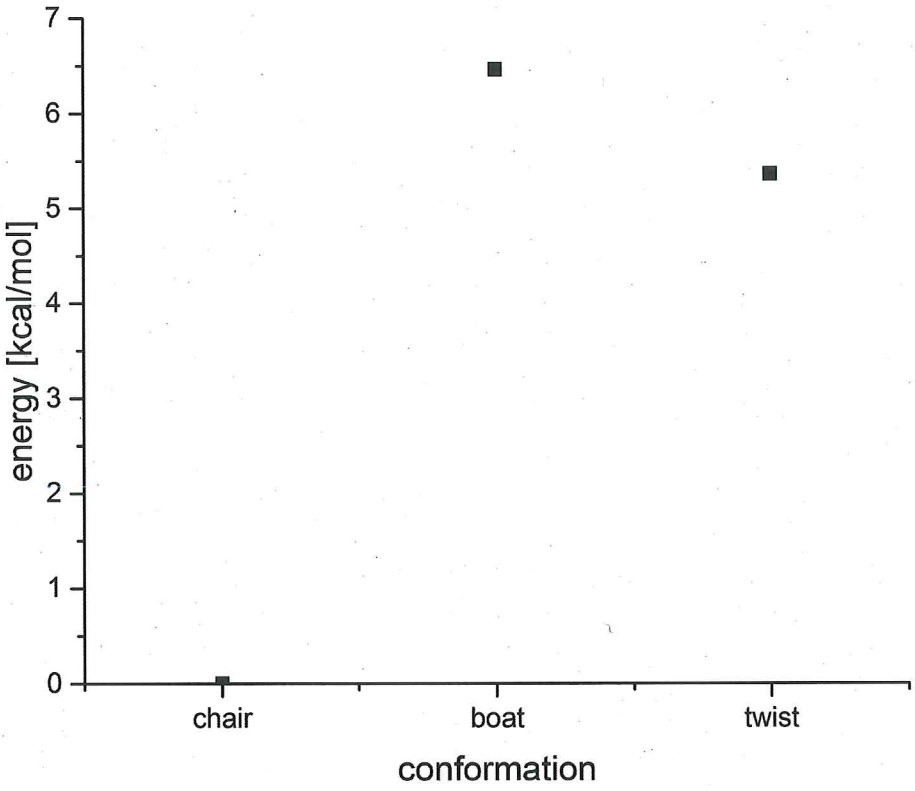


Chair conformation

	Bevor optimization	After optimization
Bond length C-C [Å]	1,54	1,54
Bond length C-H [Å]	1,09	1,12
Angle of atoms [°]		
C-C-C	109,5	110,9
C-C-H_{eq}	109,5	109,9
C-C-H_{ax}	109,5	109,5
H-C-H	109,5	107,1
Torsion angle [°]		
C-C-C-C	60	56,3
C-C-C-H_{ax}	60	64,5
C-C-C-H_{eq}	180	178,1
H_{eq}-C-C-H_{eq}	60	60,1
H_{ax}-C-C-H_{ax}	180	174,6
H_{eq}-C-C-H_{ax}	60	57,2
energy [kcal/mol]	10,14	6,55
RMS gradient [kcal/Åmol]	12,741	0,003

Boat conformation

	Bevor optimization	After optimization
H7-H13 distance[Å]	2,05	2,33
energy [kcal/mol]	14,17	13,01
RMS gradient [kcal/Åmol]	1,757	0,010
Torsion angle [°]	56,3	52,5



Fulleren C60

	1,2-addition (6,6-bond)	1,2-addition (5,6-bond)	1,4-addition
MM+			
energy [kcal/mol]	273,43	269,45	270,57
rel. energy [kcal/mol]	3,98	0	1,12
EHT			
energy [kcal/mol]	-97592,34	-97576,72	-97589,02
rel. energy [kcal/mol]	-15,62	0	-12,3
DFT			
Energy [eV]	-2,86 x 2	-2,43 x 2	-2,69 x 2
energy [kcal/mol]	65,95	56,04	62,03
rel. energy [kcal/mol]	9,91	0	5,99

Don't forget the negative sign!

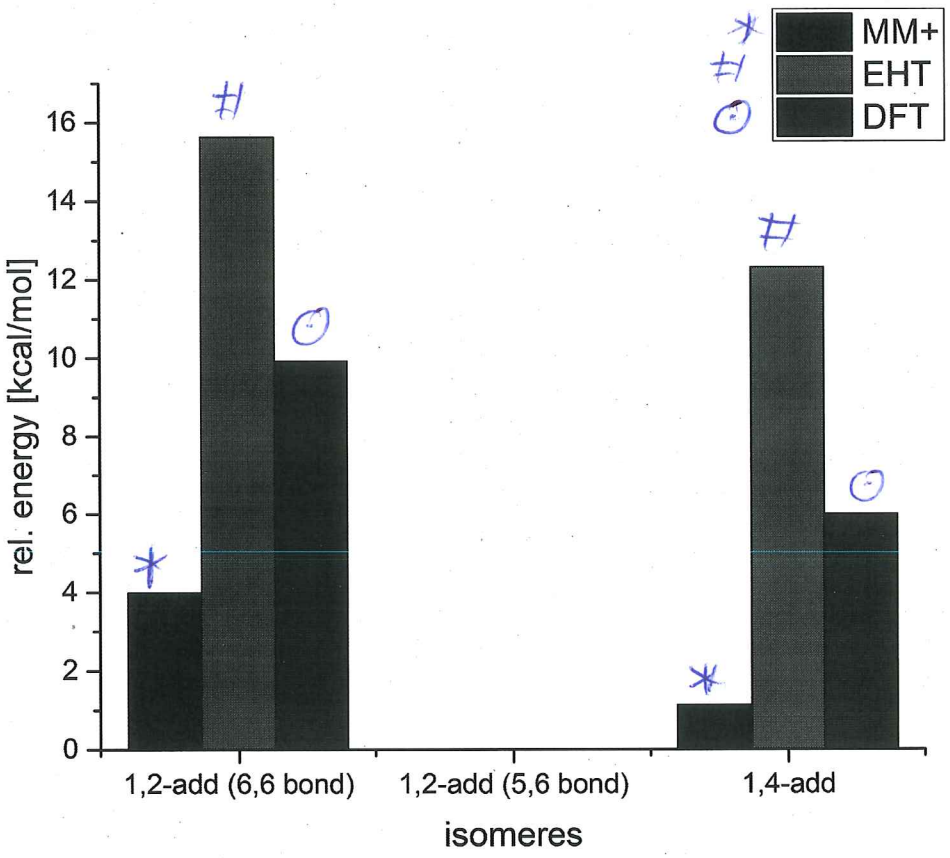
In the paper, the averaged bond energy is defined as $\frac{1}{n}\{E(C_{60})+nE(H)-E(C_{60}H_n)\}$. Here $n=2$, and if we set $E(C_{60})+nE(H)=0$, there should be a negative sign when calculating $E(C_{60}H_n)$.

So the energy sequences are:

MM+ : [1,2]-[5,6] < [1,4] < [1,2]-[6,6]

EHT } : [1,2]-[6,6] < [1,4] < [1,2]-[5,6]
DFT }

EHT is consistent with DFT, while MM+ gives the wrong results.


MM+
EHT
DFT
rel. energy [kcal/mol]
0
2
4
6
8
10
12
14
16
1,2-add (6,6 bond)
1,2-add (5,6 bond)
1,4-add
isomeres

1.55		decimal
	Å	2
	°	1
	kcal/mol	2
	grad	3

grad = [kcal/Å mol]

part I

C_6H_{12} (unoptimized)

	C_1-C_2	C_2-C_3	C_3-C_4	C_4-C_5	C_5-C_6	C_6-C_1	C-H
Bond length	1,54 Å	1,54 Å	...	...	...	...	1,09 Å
Bond angle	109,5°	...	...	...	...	...	109,~~71~~5°
~~Torsion angle~~							

Torsion angle $C_6-C-C-H_{axial}$: -60,0°
$C-C-C-H_{equatorial}$: 180,0°
C-C-C-C : 60°

$H_{eq}-C-C-H_{eq}$: 60°
$H_{ax}-C-C-H_{ax}$: 180°
$H_{eq}-C-C-H_{ax}$: -60°

1.6 Energy 10,14 kcal/mol , gradient=12,741

1.7 Energy 6,55 kcal/mol , gradient=0,003

C_6H_{12} (optimized)

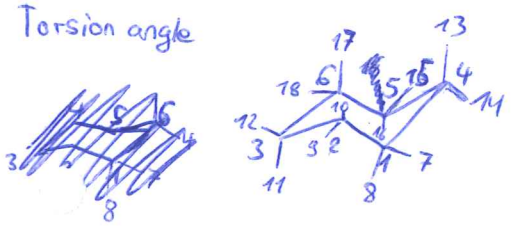
Bondlength C-C : 1,54 Å C-H: 1,12 Å

~~Bond~~ angle of atoms H-C-H: 107,09~~1~~°
$H_{ax}-C-C$: 109,46~~1~~°
C-C-C: 110,89 ~~10,83~~~~1~~°
$H_{eq}-C-C$: 109,93~~1~~°

(Torsion angle C-C-C-H_{ax} : -64,5~~8~~°
C-C-C-H_{eq} : 178,1°
C-C-C-C : 56,3°

$H_{eq}-C-C-H_{eq}$: ~~178,1~~ +60,1°
$H_{ax}-C-C-H_{ax}$: -57,2°
$H_{eq}-C-C-H_{ax}$: 60,1°)

Torsion angle



1-2-3-11 : 64,5°
1-2-3-12 : -178,1°
8-1-14-14 : -57,2°
9-2-1-7 : -60,1°
8-1-2-10 : 174,6°
8-1-2-3 : -64,5°
1-4-5-15 : 178,1°
7-1-2-3 : 178,1°
5-4-1-2 : -56,3°
6-5-4-1 : 56,3°

8-1-4-13 : -174,6°
7-1-4-14 : 60,1°
7-1-4-13 : -57,2°
7-1-2-10 : 57,2°
8-1-4-5 : 64,5°
8-1-2-9 : 57,2°
1-4-5-16 : -64,5°
7-1-4-5 : -178,1°
4-1-2-3 : 56,3°
1-2-3-6 : -56,3°

1.9 H7-H13 : 2,05 Å
5-4-3-2 : 56,3°
3-2-1-6 : -56,3°

Energy = 14,17 kcal/mol
gradient = 1,757

1.10 (optimization) Energy = 13,01 kcal/mol , gradient = 0,010 , H7-H13 : 2,33 Å
5-4-3-2 : 52,5° 3-2-1-6 : -52,5°

1.11 Energy = 14,31 kcal/mol , gradient = 13,012

1.12 (optimized) Energy = ~~11,31~~ kcal/mol , gradient = 0,008

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part II

2.4 optimized Energy = 273,43 $\frac{kcal}{mol}$ gradient = 0,065

2.5 EHT Energy = -97592,34 $\frac{kcal}{mol}$ (between two 6-Rings)

2.6 1,2-Add : (between 5-ring and 6-ring) optimized Energy = 269,45 $\frac{kcal}{mol}$ gradient = 0,0001 (MM+)

EHT : Energy = -97576,12 $\frac{kcal}{mol}$

2.7 optimized (1,4-Add) Energy = 270,57 $\frac{kcal}{mol}$, gradient = 0,061

EHT Energy = -97589,02 $\frac{kcal}{mol}$