Semi Empirical Study of a System Containing a Six-membered Ring

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Semi-empirical AM1 SCF-MO calculations have been used to find the structure optimization and conformational interconversion pathways of a system containing a six-membered ring. The system has the two symmetrical energy-minimum conformations, chair and twist. The chair conformation has the most stable geometry. Some quantum parameters such as HOMO and LUMO energy, the chemical hardness and chemical potential are discussed.

Key words: Six-membered Rings; Conformational Analysis; AM1 Calculations; Quantum Chemical Study.

1. Introduction

With the rapid development of computer hardware and software, computational chemistry has become a popular tool for the study of molecules and their chemical reactions [1 – 8]. Quantum mechanical calculations are also very important, because they provide a better basis for understanding the conformational changes of a molecule. Among the quantum mechanical methods, the semiempirical approach is known for its high speed and relatively high accuracy. Perhaps the most familiar semiempirical method is the Austin Model 1 (AM1), developed by Dewar and coworkers [9].

The conformational behavior of six-membered rings has attracted considerable attention for a recent review [10]. Although six-membered rings preferentially adopt the chair conformation, some of them can choose the twist conformation [11 – 13].

Previously we reported the synthesis and X-ray crystal structure analysis of the molecular complex 5-(1-oximidoethyl)-2,2,5-trimethylhexahydropyrimidine and butanedione monoxime (see Fig. 1) [14]. X-ray results indicate that the perhydropyrimidine group (**I**) adopts the chair conformation. The present work aims to examine the different conformations of (**I**), using Semi-empirical AM1 SCF-MO calculations with the purpose of obtaining information on the lowest-energy conformers. Thus, the geometric parameters can be compared with those obtained from experimental work. The chemical hardness and chemical potential were also calculated, and the principle of maximum hardness has been tested.

2. Method of Calculation

Semi-empirical calculations were carried out using the AM1 method with the MOPAC 6.0 program [15]. Energy minimum geometries were found by minimizing the energy, with respect to all geometrical coordinates without any symmetry constraints. The structures of the transition-state geometries were obtained using the optimized geometries of the equilibrium structures according to the procedure of Dewar et al. [16] (Keyword SADDLE). The local energy minima and transition-states on the potential energy surface were found using the Keyword FORCE [17].

The chemical hardness (η) and chemical potential (μ) were calculated using the energies of the highest (HOMO) and lowest (LUMO) occupied molecular orbital. The chemical hardness and chemical potential are expressed with an orbital basis as

$$\eta = \frac{I-A}{2}, \quad \mu = \frac{I+A}{2}$$

where $I = E_{\mathrm{HOMO}}$ and $A = E_{\mathrm{LUMO}}$, I and A are the ionization potential and electron affinity of a molecule [18].

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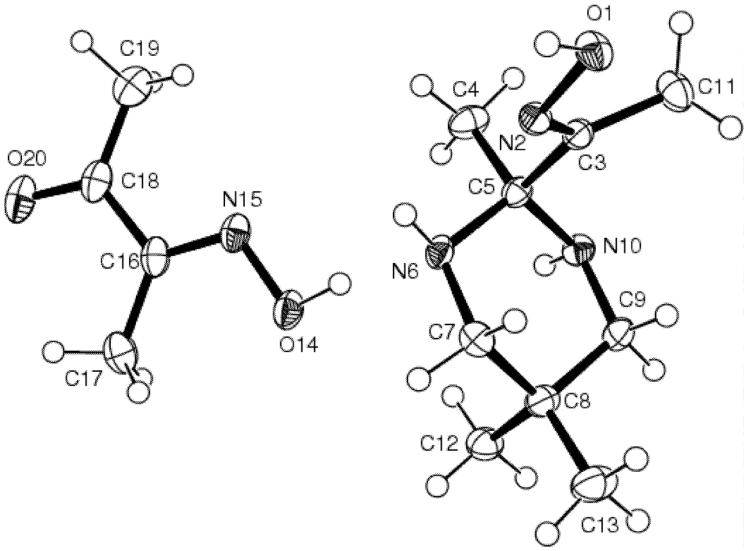


Fig. 1. The molecular structure and atomic labeling scheme of the title compound. Displacement ellipsoids are plotted at the 50% probability level (ORTEP-3) [31].

Table 1. The values of selected optimized geometries of the chair, twist and boat conformers of (**I**). Experimental values [14] are shown for comparison. Bond lengths, *r*, are given in Å, bond angles, α, and dihedral angles, τ, are both given in degrees.

Geometric parameter	Chair	Twist	Boat	Experimental
r(C5-N6)	1.49	1.49	1.48	1.48
r(N6-C7)	1.45	1.45	1.44	1.48
r(C7-C8)	1.54	1.54	1.54	1.53
r(C8-C9)	1.54	1.55	1.54	1.53
r(C9-N10)	1.45	1.45	1.44	1.47
r(N10-C5)	1.48	1.49	1.48	1.47
α(C5-N6-C7)	114.3	113.3	119.1	113.5
α(N6-C7-C8)	112.6	114.7	116.5	111.8
α(C7-C8-C9)	107.0	108.9	105.9	107.2
α(C8-C9-N10)	114.9	116.2	115.1	113.9
α(C9-N10-C5)	113.5	114.2	121.0	112.6
α(N10-C5-N6)	111.8	114.2	117.0	110.9
τ(C5-N6-C7-C8)	−55.1	55.2	27.7	−56.0
τ(N6-C7-C8-C9)	53.3	−45.0	−54.4	53.3
τ(C7-C8-C9-N10)	−52.4	−7.5	−52.3	−53.8
τ(C8-C9-N10-C5)	52.1	50.4	−25.2	55.3
τ(C9-N10-C5-N6)	−48.5	−50.0	−5.6	−52.9
τ(N10-C5-N6-C7)	51.2	−11.2	4.2	54.2

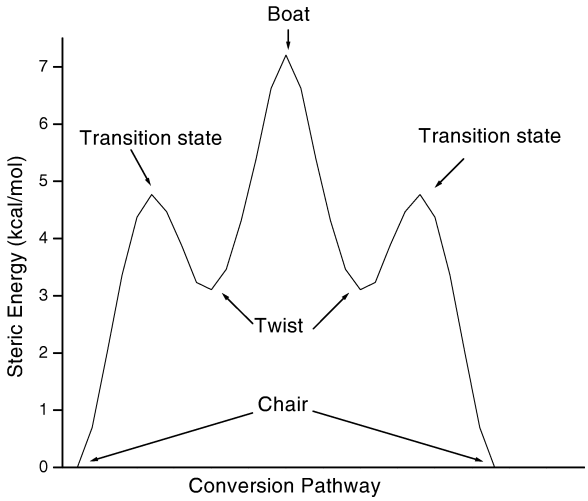
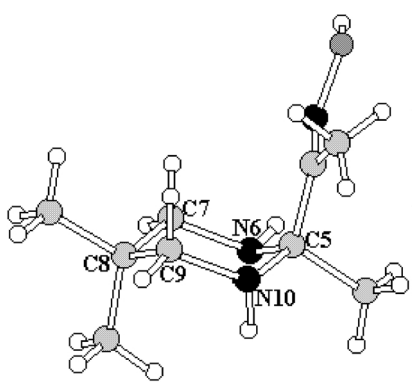


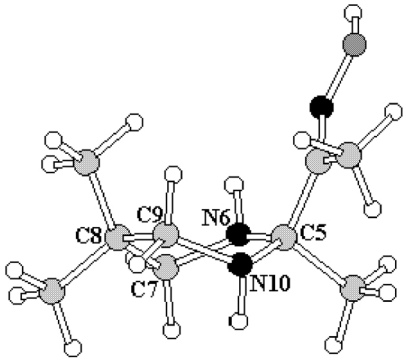
Fig. 2. Calculated AM1 standard strain energy (kcal/mol) profile for conformational interconversion of the perhydropyrimidine group (**I**).

3. Results and Discussion

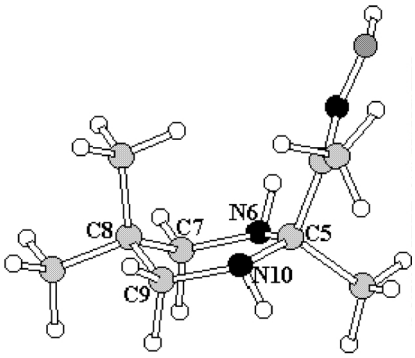
The results of semi-empirical AM1 calculations for structure optimization and conformational interconversion pathways (**I**) are shown in Figure 2 and Table 1. The energy surface for the interconversion of energy-minimum conformations of (**I**) was investigated in detail by changing different torsional angles. Seven geometries (four energy minima and three transition states) were found to be important in the description of the conformational properties of (**I**). The chair, boat and twist conformations of (**I**) are shown in Fig. 3 along with the atom numbering used. The most stable conformation of (**I**) is found to be chair conformation in agreement with available experimental data [14]. The heat of formation and zero point energy, total, electronic, core-core repulsive, HOMO and LUMO energies, the chemical hardness (η) and chemical potential (μ) for the chair, twist and boat conformers of (**I**) are shown in Table 2. The chair conformation is calculated to have the lowest heat of



(a)



(b)



(c)

Fig. 3. Chair (a), boat (b), and twist (c) conformations of (**I**).

Table 2. Calculated heat of formation and zero point energy (ZPE) (kcal/mol), total, electronic, core-core repulsive, HOMO and LUMO energies, HOMO-LUMO energy gaps (ΔE), chemical hardness (η) and chemical potential (μ) (eV) for the chair, twist and boat conformers of (**I**).

AM1	Chair	Twist	Boat
ΔH_f^0	−10.56	−7.46	−3.35
$\Delta\Delta H_f^{0a}$	0.0	3.10	7.21
ZPE	182.07	181.81	180.93
Total energy	−2354.56	−2354.43	−2354.24
Electronic energy	−14646.98	−14579.94	−14620.70
Core-Core repulsive energy	12292.42	12225.51	12266.46
HOMO	−9.40	−9.21	−9.01
LUMO	1.06	1.09	1.16
ΔE	10.46	10.30	10.17
η	5.23	5.15	5.09
μ	−4.17	−4.06	−3.93

[a] The standard strain energy in each geometry of a molecule is defined as the difference between the standard heats of formation (ΔH_f^0) for that geometry and the most stable conformation of the molecule [30].

formation (ΔH_f^0). As the twist form has a higher (by $\approx$ 3.10 kcal/mol) ΔH_f^0 than the chair conformation, it is not expected to be significantly populated at room temperature.

The structural parameters for chair, twist and boat conformations of (**I**) are given in Table 1. It can be seen that N–C and C–C bond distances are in very good agreement with experimental values, being the absolute error about 0.01 Å for the chair, twist and boat conformers. Bond angles in the chair conformer are in excellent agreement with experimental data being the absolute error (less than 1.00).

The highest occupied molecular orbital, HOMO, and the lowest unoccupied molecular orbital, LUMO, of a molecule are called the frontier orbitals. It was Fukui [19] who first noticed the prominent role played by HOMO and LUMO in governing chemical reactions. It has been revealed by recent investigation that the gap in energy between the HOMO and LUMO is an important stability index [20–22]. A large gap implies high stability and small gap implies low stability. The high stability in turn indicates low chemical reac-

tivity and small gap indicates high chemical reactivity. The energy and symmetry type of, and the charge distribution in HOMO, and the energy and symmetry type of LUMO are known to determine the structures of molecules [23 – 25]. The index of chemical reactivity and stability of a molecule is its chemical hardness. Increase in hardness increases the movement of the system towards a more stable configuration and when a chemical species moves away from its equilibrium configuration its hardness value decreases. When a system evolves towards a state of greater hardness, its stability increases.

The chemical hardness (η) and chemical potential (μ) have been calculated for chair, twist and boat conformations of (**I**) using the molecular orbital energies, and the values are summarized in Table 2. According to the maximum hardness principle (MHP) the molecules arrange themselves with maximum hardness [26 – 29]. The chair conformation has the maximum hardness value, which is the minimum energy conformation. Therefore, again we concluded that the minimum energy conformation has maximum hardness value in accordance to the Pearson's maximum hardness principle.

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