Research article

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Theoretical study of the effect of internal strain on the bond length and rate of hydrolysis in cyclic amides

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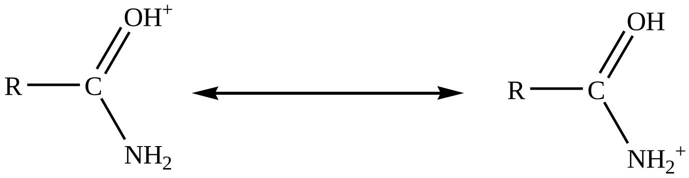
Abstract

The internal strain in cyclic amides are explained as a factor of resonance that are effected on the bond length C-N and are a major factor of rates of hydrolysis. The cyclic amides in this study are optimized by Gaussian program and the bond length of C-N in the rings are studied by HF/6-31G*.

Keywords: cyclic amides; bond length; relative rate hydrolysis; resonance; internal strain

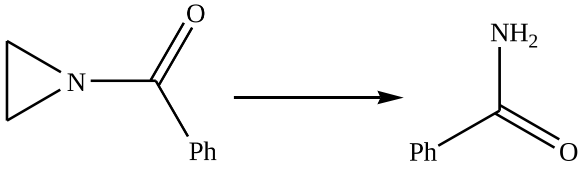
Introduction

The mechanism for acid-catalyzed hydrolysis of amides to carboxylic acids and amines requires considerably more of the chemistry of amides [1]. An important feature of the chemistry of amides is that the most basic site in an amide is the carbonyl oxygen very important form is present [2-4]. The major factor that are contributed to the stability of the O-protonated form is the π- electron delocalization over the O-C-N system [5] (scheme 1).



Scheme 1. Delocalization of electrons in amides

The relative rate of hydrolysis of the (aziridin-1-yl)(phenyl)methanone **(1)** is 10^5 faster of The Benzamide **(2)[**6] (scheme 2).



1 **2**

Scheme 2. Decrease of relative rate of hydrolysis in cyclic amides

In cyclic amides with the nitrogen atom that is part of a ring, rate of hydrolyze depend on the bond angle strain in cyclic amides. The change of internal strain is effected on the resonance stabilization of the carbonyl group and the bond length of C-N. the effect of bond length is calculated and explained in this paper.

Calculations

The Ab intio calculations have been Performed on a Pentium-4 based system using GAUSSIAN 98 progeram. The restricted Hartree–Fock calculations with the split-valence 6-31G* basis set were used in these calculations [7].

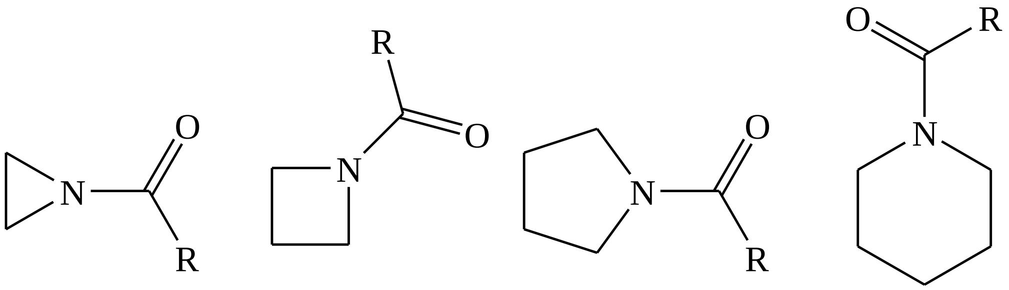
Results and Discussion

The largest distortions from natural bond angels are found in three-membered rings [8]. The effects of bond-angle distortion are minimized in cyclic amides by changes in hybridization at atoms forming the rings.

In the three-membered cyclic amides, the bond forming the ring are not made up of sp^3 hybrids, but have more P character. The result is that the inter orbital angle distortion is much less than the inter nuclear angle distortion, because as the p character of the ring bonds increases, the natural inter orbital angle reduces from the sp^3 value. This in ring bonding also affects other bonds formed by the ring atoms; those to the substituted. These have much more S character than normal.

The change in hybridization is associated with a change in electronegativity, The greater the S character of a nitrogen orbital, the greater is its electronegativity. Thus, the decrease resonance stabilization of the carbonyl group, wich is opposed by the delocalization of the nitrogen lone pair with high electronegativity are effected on the C-N bound length [9].

In our current study, extensive calculations the effect of bond length C-N in cyclic amides (scheme 3) are presented in table1.



a **b** **c** **d**

1 R= H
2 R= CH3
3 R= CH3CH2

Scheme 3. Cyclic amides with a nitrogen atom in rings

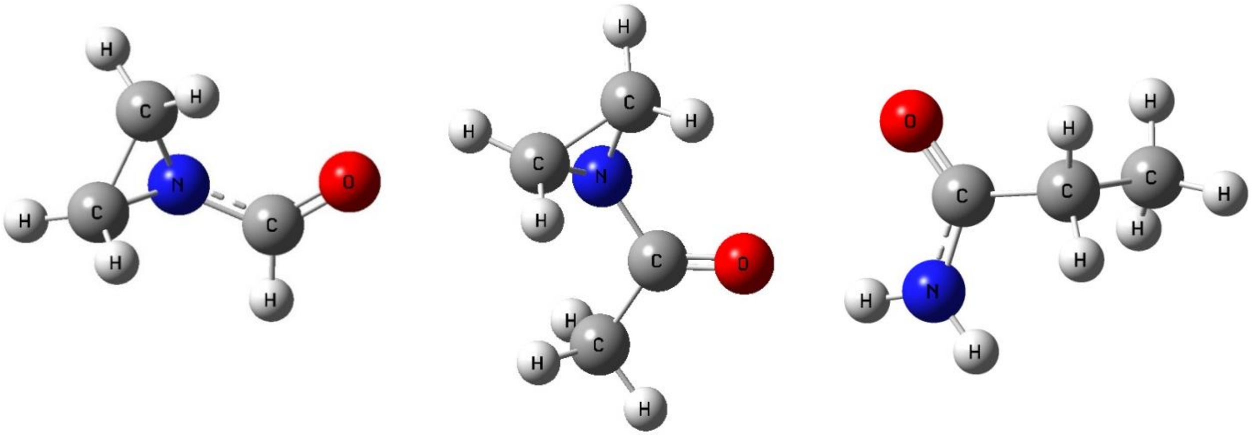
Table 1. HF/6-31G*calculations for cyclic amides.

Name	Bond length of C-N (A^0)
Formamide*	1.350
1a	1.370
1b	1.351
1c	1.346
1d	1.341
Acetamide*	1.361
2a	1.390
2b	1.369
2c	1.353

2d	1.341
Propionamide[*]	1.365
3a	1.394
3b	1.367
3c	1.353
3d	1.342

*In the table formamide and acetamide and propionamide are studied as references.

An important notice is that the bond in 1b is sample bond because the hydrogen group is less than electronegative of methyl group **(figure 1)**.



1a **2a** **3a**

Fig. 1. The effect of electronegativity of R in cyclic amides by geometries determined by Hartree-Fock level

These calculations are showed that 1-(aziridin-1-yl)ethanone **(1a)** and aziridine-1-carbaldehyde **(2a)** have the tallest bond length in C-N and piperidine-1-carbaldehyde **(1d)** and 1-(piperidin-1-yl)ethanone **(2d)** have the smallest bound length in C-N.

Conclusion

In the cyclic amides with the nitrogen atom that is part of a small ring, the S character in nitrogen atom is greather of normal, thus the electronegativity is high and the bond length in C-N is tall, thus the rate of hydrolysis is fast.

But in amides with big rings the S character and the electronegativity in nitrogen atom is normal, thus is existed the resonance in carbonyl group with nitrogen and the bond length of C-N is smallest of small rings, and rate of hydrolysis in theme is lowest.

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