

## CONFORMATION – CONFIGURATION CORRELATION IN HEMIAMINALS.

*Anna Kwiecień, Maciej Barys, Zbigniew Ciunik, Krzysztof Drabent*  
*Faculty of Chemistry, University of Wrocław, 14 F. Joliot-Curie St, 50-383 Wrocław*  
*aniuta04@gmail.com*

Hemiaminals ( $\alpha$ -amino alcohols) –  $R_2C(OH)NR_2$ , are chemical compounds obtained in the addition reaction of ammonia, or of primary or secondary amines to the carbonyl group of aldehydes or ketones. These compounds generally are referred to be unstable[1] due to the subsequent process of elimination of a water molecule and forming compound with double C=N bond (Fig.1.).

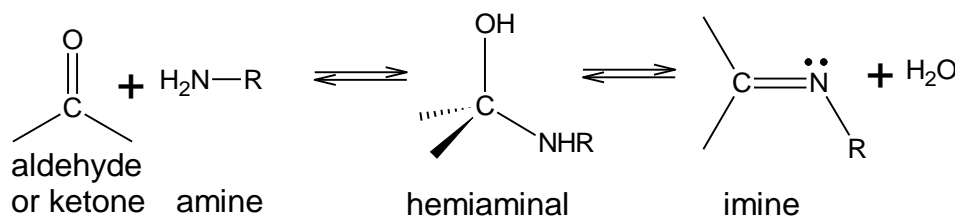


Fig.1. Scheme of the addition reaction of the primary amine to the carbonyl group.

Recently, we have studied the reaction between 4-amino-1,2,4-triazole and substituted benzaldehydes in an acetonitrile solution under neutral conditions. For nitrobenzaldehyde derivatives stable hemiaminals were obtained[2]. The molecular structures of obtained compounds consist of phenyl (Ph) and triazole (Trz) rings directly linked through the C1–C14–N4–N3 chain of atoms. In the hemiaminals, the N4 and C14 atoms have  $sp^3$  hybridization and both exhibit stereogenic centers.

In the crystal structures of the title hemiaminals, two molecular conformations — stretched and twisted — are observed (Fig.2.).

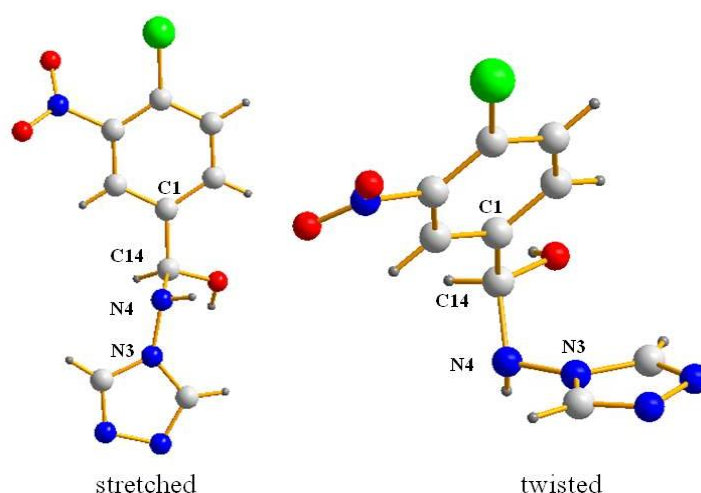


Fig.2. Stretched and twisted conformations, as well as the numbering system used for the hemiaminals.

As mentioned above, the hemiaminals studied here have two stereogenic centers, at the N4 and C14 atoms, but only two of the four possible enantiomers are observed for each conformer. In the case of the stretched ones, only the *RS* and *SR* exist in solid state, while only the *RR* and *SS* enantiomers are observed for the twisted ones.

Geometrical analysis of both stereogenic centers in all hemiaminals shows that this lone pair and a hydroxyl group have an *ap* orientation. The main reason for this observation lies in the repulsive stereoelectronic effect, similar to the anomeric effect. This observation should be correlated with the conformation and configuration of hemiaminals (Fig.3).

Transformation of a stretched molecule into a twisted one may be realized in the course of two low energetic processes[3]: rotation about the C–N single bond and inversion of configuration on the N atom. During the possible rotation about the C14–N4 bond, the lone electron pair on the N4 atom approaches the hydroxyl group but the repulsion between them causes an inversion of configuration on the nitrogen atom.

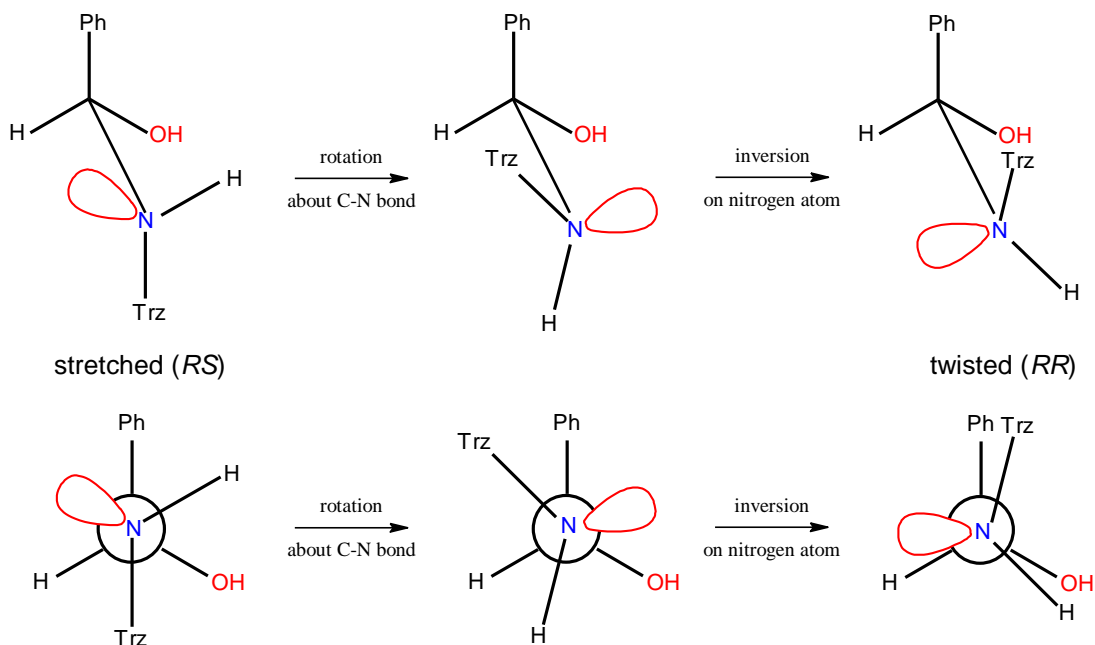


Fig.3. Conformational and configurational changes in hemiaminals.

1. March J., Smith M. B. *March's Advanced Organic Chemistry: Reactions, Mechanisms, and Structure*, John Wiley & Sons, Inc., 6<sup>th</sup> edition, 1281 (2007).
2. Barys M., Ciunik Z., Drabent K., Kwiecień A. *New J. Chem.* **34**, 2605 (2010).
3. McMurry, J. *Organic Chemistry*, Brooks and Cole, 5<sup>th</sup> edition, 981 (2000).