

MS28-1-12 On the selectivity of methylation of the amidine system and stereoisomerism of 3-alkylated derivatives of 5-methoxycarbonylmethylidene-4-phenylimino-1,3-thiazol-2(5H)-one
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A. Pyrih ¹, M. Jaskolski ², R. Lesyk ³, A. Gzella ⁴

¹Adam Mickiewicz University in Poznań - Poznań (Poland) - Poznań (Poland), ²Institute of Bioorganic Chemistry, Polish Academy of Science - Poznań (Poland), ³Danylo Halytsky Lviv National Medical University - Lviv (Ukraine), ⁴Poznań University of Medical Sciences - Poznań (Poland)

Abstract

The following four methylated derivatives of 5-methoxycarbonylmethylidene-4-phenylamino-1,3-thiazol-2(5H)-one, with the potential to form $\text{N}=\text{C}-\text{NH} \leftrightarrow \text{NH}-\text{C}=\text{N}$ tautomeric equilibria, were synthesized and studied by X-ray crystallography in order to determine the selectivity of methylation of the amidine system:

3-methyl-5-methoxycarbonylmethylidene-4-phenylimino-2-thiazolidione; 3-methyl-5-methoxycarbonylmethylidene-4-(4-bromophenylimino)-2-thiazolidione; 3-methyl-5-methoxycarbonylmethylidene-4-(4-chlorophenylimino)-2-thiazolidione; 3-methyl-5-methoxycarbonylmethylidene-4-(4-fluorophenylimino)-2-thiazolidione.

The crystal structures show that the methylation takes place in each case selectively at the nitrogen atom of the heterocycle. It was found that the presence of a bulky methyl group in that position causes a change in the conformation of the molecule with respect to the substrates - 5-methoxycarbonylmethylidene-4-phenylamino-2-thiazolinones, which are characterized by a very stable synperiplanar conformation. At the same time, due to the shift in the position of the double bond in the amidine group, the molecules of all four products adopt the E configuration. The latter observation is particularly interesting, as this is the first time it has been reported for 4-phenylamino-1,3-thiazol-2(5H)-one derivatives. It is also worth noting that in the newly prepared methylated derivatives of 5-methoxycarbonylmethylidene-4-phenylimino-2-thiazolidinone, the thiazolidinone and phenyl rings are approximately perpendicular, in contrast to the coplanar orientation in the substrate molecules. The flat 5-methoxycarbonylmethylidene moiety in both, the substrate and products molecules has the Z configuration and lies approximately in the plane of the heterocycle.

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