

CONFORMATIONAL STUDY OF THE 1,3 N-N DISUBSTITUTED BENZOTRIAZOLIUM BROMIDE SALTS

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ABSTRACT: This paper's goal is to make a conformational study of the 1,3 N-N disubstituted benzotriazolium bromide salts. The optimised method of salt was used. Two isomeric carbanion disubstituted benzotriazolium ylides were obtained in a mixture, in the proportion 3:1. To observe those ylides, as well as the size of their rapport, the ¹H-RMN spectra will be used.

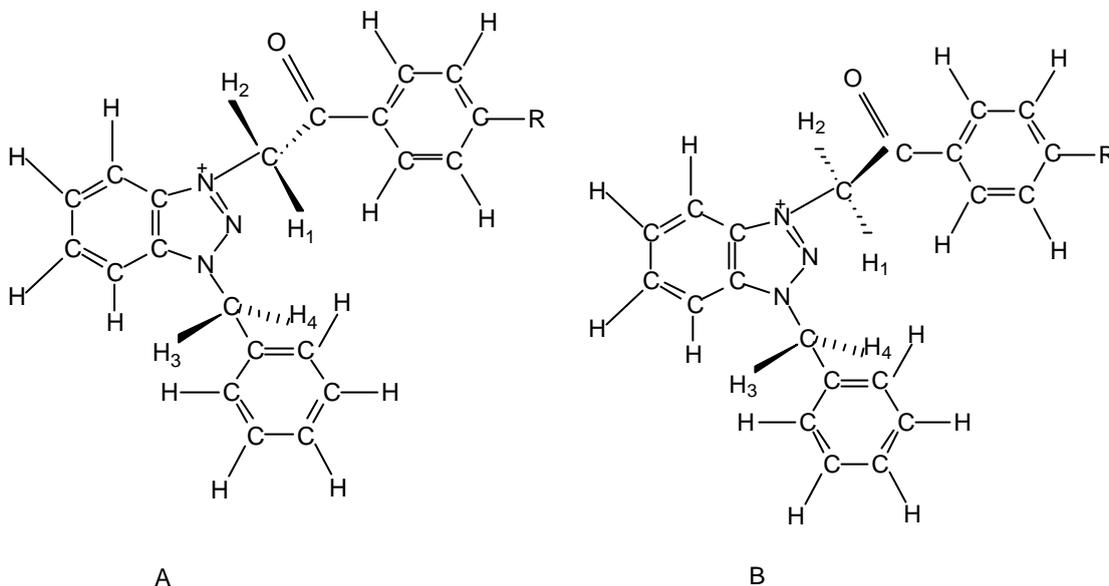
KEYWORDS: *benzotriazolium, benzotriazolium salts, carbanion mono- and disubstituted ylides.*

INTRODUCTION

The salts were obtained by a classical method which is often used in the final synthesis of the ylidical compounds. The methods that were used in the conformational study were the semi empirical methods of the quantum mechanics – the AM1 and PM3 methods.

EXPERIMENTAL

For benzotriazolium salts that contains benzyl and phenacyl radicals linked with benzotriazolium there are two possible conformations: A and B.



- a: R=H
 b: R=OCH₃
 c: R=Cl

Scheme no. 1

The difference between these conformations is the position of the phenacyl fragment regarding the benzotriazolium ring.

A structure has the phenacyl fragment situated beyond and the B structure has it in the front. The multiconformational study was made at the level of every simple bond from the two fragments. The minimum that was obtained in the first complete rotation is used as a basis in the beginning of the next rotation, and so on till is completely covered the domain of every simple bond that can give a rotation. The value of the rotation plan was 15° and the conformers choose was made upon the reaction enthalpy ΔH .

Table no.1 Forming heat

Salt	Method	Structure A	Structure B
1 a.	AM1	291.373	291.698
	PM3	254.852	255.290
1 b.	AM1	252.141	252.484
	PM3	215.815	215.400
1 c.	AM1	285.894	286.247
	PM3	249.318	249.635

RESULTS AND DISCUSSIONS

The developed study has shown insignificant rotation barriers and small differences regarding the forming heats of the two conformers A and B.

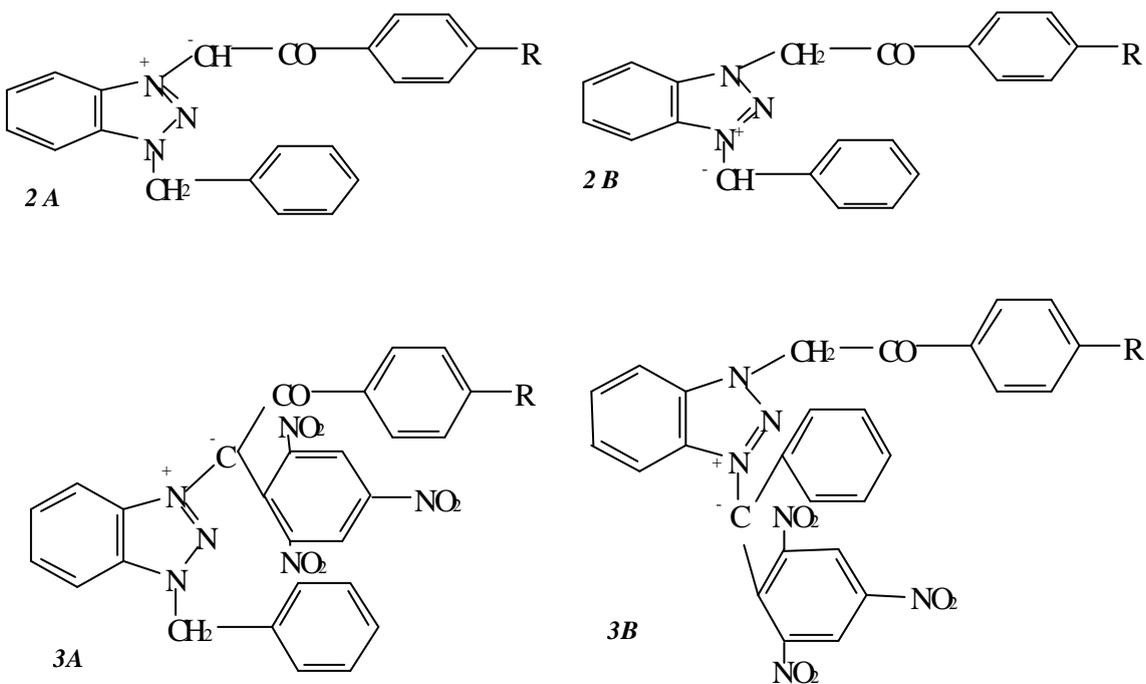
From the obtained data, the conclusion is that the 1 a, b, c salts should be regarded as equilibrium structures around A and B conformations. All the rotation barriers on the two structures A and B are below 3 kcal/mol.

The evaluation of those salts' chemical behavior in order to obtain carbanion monosubstituted ylides 2 was made only for A type conformations.

In Table 2 there are presented the total atomic charges of the methylenic hydrogens, calculated by the AM1 and PM3 methods.

Table no. 2 Total atomic charges

Salt	Method	Charges	H1	H2	H3	H4
1a.	AM1	Electrostatic	0.171	0.166	0.162	0.162
		Mulliken	0.163	0.152	0.133	0.144
	PM3	Electrostatic	0.184	0.138	0.094	0.126
		Mulliken	0.132	0.115	0.095	0.120
1b.	AM1	Electrostatic	0.170	0.166	0.169	0.171
		Mulliken	0.161	0.150	0.133	0.146
	PM3	Electrostatic	0.158	0.112	0.105	0.089
		Mulliken	0.130	0.114	0.107	0.092
1c.	AM1	Electrostatic	0.157	0.150	0.176	0.179
		Mulliken	0.163	0.152	0.133	0.146
	PM3	Electrostatic	0.148	0.134	0.101	0.105
		Mulliken	0.131	0.115	0.093	0.108



Scheme no. 2 Carbanion monosubstituted ylides (2A, 2B) and carbanion disubstituted ylides (3A, 3B)

Despite it was expected the mobility of the methylenic hydrogens from the phenacyl fragment to be bigger as the one of the methylenic hydrogens from the benzyl fragment, the numeric results obtained and shown in Table 2 quash that idea.

CONCLUSIONS

In conclusion, due to the similar (closed) mobility of the hydrogen atoms from the methylenic groups from benzyl and phenacyl fragments, the carbanion monosubstituted ylides 2A and 2B can be obtained as reaction intermediates. Also, treating the salts with picryl chloride in the presence of T.E.A., can result in obtaining in the final of two isomer carbanion disubstituted ylides 3A and 3B.

Next, experimentally should be put in a conspicuous manner the existence of the two isomer ylides, with a little help from the ^1H -RMN spectra. This conclusion is also based on the fact that in the specialty literature the existence of tautomere carbanion disubstituted ylides from the triazole class had been mentioned.

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