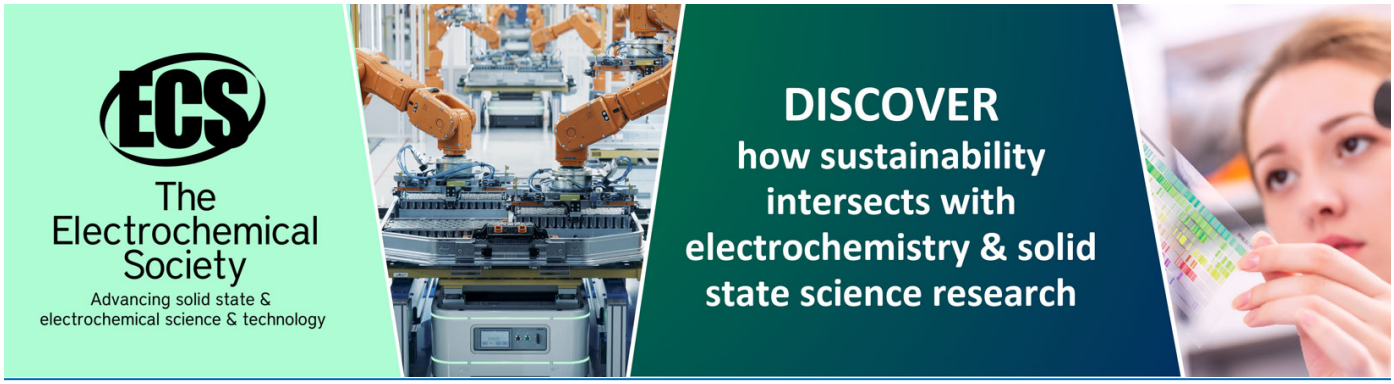
Outlook of C-substituted benzotriazoles application as corrosive inhibitors



Outlook of C-substituted benzotriazoles application as corrosive inhibitors

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Abstract. In this work the method of the synthesis of C-substituted benzotriazoles is reported. Several target compounds were synthesized from unsubstituted benzotriazole by the diazotation reaction. Quantum-chemical calculations of basic electronic properties of the studied molecules were performed. It was shown, that introducing of halogen atom or thiocyano-group decreases the energies of frontier orbitals.

1. Introduction

Corrosion processes lead to the decreasing of the operating properties of metal construction, and can cause their destruction. Only direct losses from corrosion are about 3-5% of Gross Domestic Product (GDP) of industrial countries yearly [1]. Corrosion products and toxic reagents, formed by industrial equipment's and pipelines' crashes, affect environment, causing severe damages. This makes the development and application of corrosion protection an important part of industrial sciences.

One of the most efficient methods of corrosion inhibition is the usage of corrosion inhibitors [2]. Various classes of inorganic and organic compounds possess anticorrosive activity. Derivatives of organic heterocycles are the compounds of big interest due to their ability to adsorb upon metal surfaces and to form strong complexes with metal ions. According to the recent studies, fused heterocycles with two or more heteroatoms demonstrate the greatest efficiency [3]. One of the most well-known corrosion inhibitor is 1*H*-benzotriazole [4-5] because of its commercial availability, low toxicity and wide range of possible applications.

Previously it was shown [6-7] that electron-donating functional groups in aromatic ring increase anticorrosive properties of the inhibitors, while electron-withdrawing decrease them. For benzotriazole mostly N-substituted derivatives are described [8], and only few reactions of C-substitution are reported [9-10]. Commonly, C-substituted benzotriazole derivatives could be obtained from correspondent ortho-phenylenediamines [11-12], but it should be mentioned, that these compounds are able to oxidase and quite expensive.

In this work we suggest a method for preparation of C-substituted benzotriazole derivatives from benzotriazole and consider their ability to inhibit corrosion processes by quantum-chemical calculations.

2. Materials and methods

Quantum-chemical calculations were performed using Gaussian09 software [13]. Structures of the studied compounds were optimized and the energies of Highest Occupied Molecular Orbitals

(HOMO) were estimated with the B3LYP method, combined with 6-311G (d, p) basic set, as it was shown [14] that this method gives the most precise results.

Started chemicals were obtained from commercial suppliers (Acros, Sigma-Aldrich). Mass-spectra of the synthesized compounds were registered on MS-30 Kratos (EI, 70eV).

3. Results

We decided to synthesize the C-substituted benzotriazoles by diazotation of 4-aminobenzotriazole. Firstly, 4-nitrobenzotriazole **2** was prepared from unsubstituted benzotriazole **1** by the reported method [9]. Then it was reduced by hydrazine hydrate in the presence of graphite [15]. By diazotation of the amine **3** we obtained 4-bromo-, 4-chloro- and 4-thiocyanobenzotraizoles (**4-6**) (figure 1). Structures of the synthesized compounds were confirmed by mass-spectroscopy.

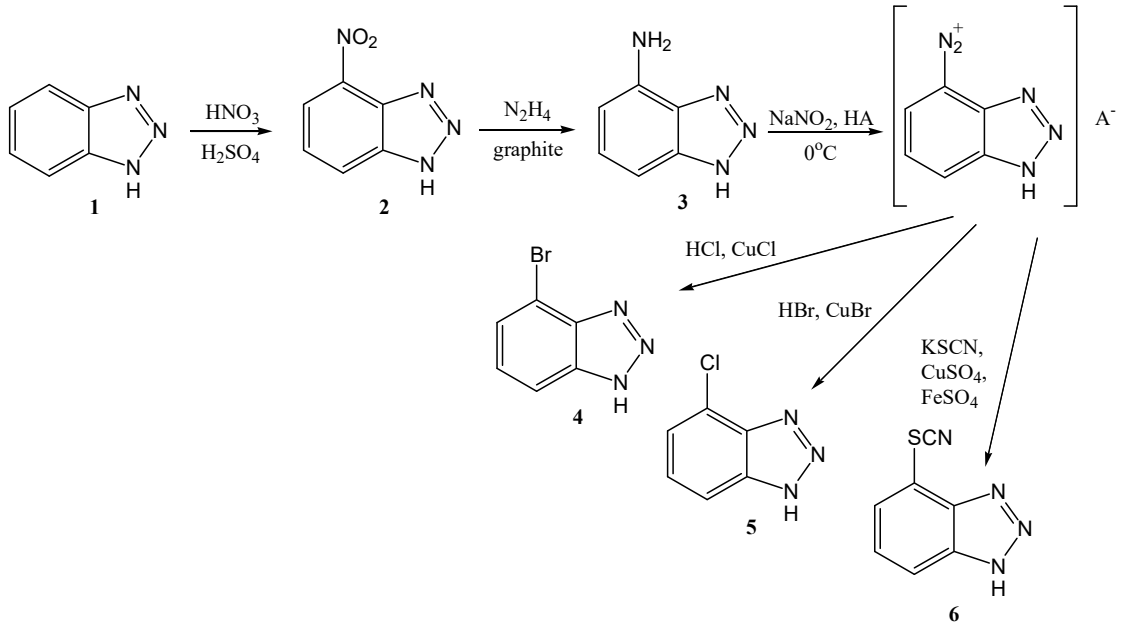

Figure 1. Scheme of the synthesis of C-substituted benzotriazole derivatives.

To estimate possible anticorrosive activity, for all considered compounds **1-6** were performed quantum-chemical calculations. Their structures were preliminary optimized, and then several basic parameters were calculated, such as dipole moment and HOMO energy (table 1), as it was reported [16] that these values correlate with the anticorrosive properties of organic compound.

Table 1. Results of quantum-chemical calculations for the studied compounds **1-6**.

Compound	Total energy, a.u.	$E_{(HOMO)}$, eV	$E_{(LUMO)}$, eV	μ, *D*
1	-395.963531	-7.163	-0.975	3.988
2	-600.508081	-7.691	-3.584	7.788
3	-451.323739	-7.093	-0.797	4.564
4	-2969.502737	-7.519	-1.200	5.100
5	-855.581620	-7.544	-1.207	5.272
6	-886.425615	-7.558	-1.534	6.013

4. Discussion

4-Aminobenzotriazole was obtained by reported method [15], but we tried to optimize the synthesis' way. Usage of zinc or tin (II) chloride in hydrochloric acid did not lead to the formation of the desired

product. With sodium dithionite in aqueous tetrahydrofuran 4-aminobenzotriazole was obtained only with poor yield (about 30%).

Diazotation of the resulting amine under common procedure of Sandmeyer reaction in the presence of copper (I) salts gave us products **4-6** with acceptable yields (about 65%). The structures of obtained compounds were confirmed by mass-spectroscopy, as it gives more information in this case than NMR-spectroscopy. Mass-spectra of **4** and **5** demonstrate typical ratio of peaks intensity that is characteristic for halogen-containing organic compounds (figure 2). Thus, for the compound **4**, the first group of peaks (with m/z equal to 197 and 199) corresponds to the molecular ions, and the second one (169 and 171) corresponds to ions that are formed by the extrusion of nitrogen.

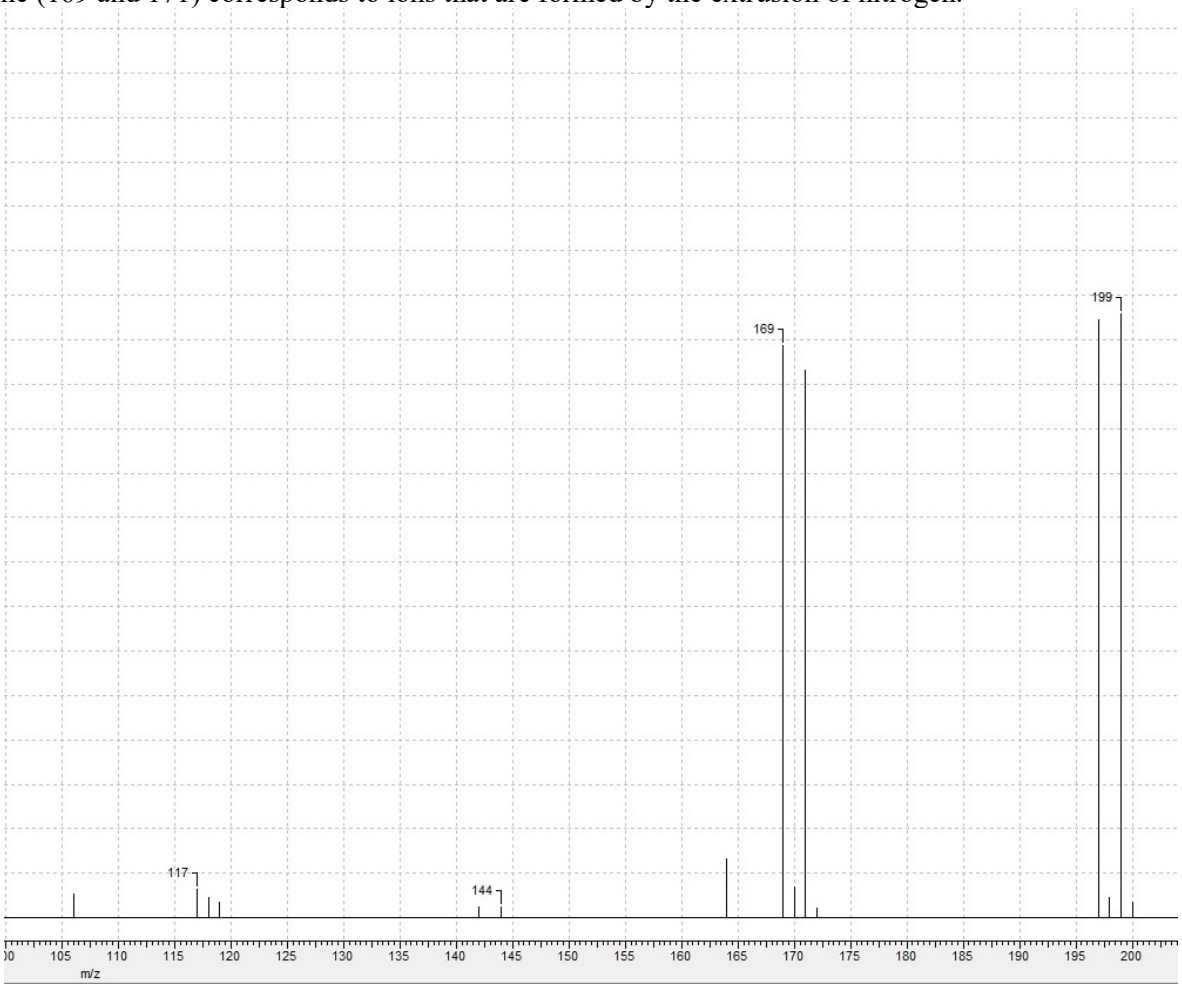

Figure 2. Mass-spectrum of the compound **4**.

Mass-spectrum of the compounds **6** shows that it is contaminated with 4-nitrobenzotriazole **2**.

To predict possible anticorrosive properties of considered compounds we performed quantum-chemical calculations of their electronic properties. As it was shown previously, the inhibitory activity of organic compounds can be predicted properly by quantum-chemical methods [17]. The most significant values are the energies of frontier orbitals and dipole moment. The higher is the energy of the highest occupied orbital (HOMO), the higher the donation of the inhibitor to metal's vacant d-orbital; the lower is the energy of the lowest unoccupied orbital (LUMO), the greater is the electron acception from the metal to inhibitor. One can see, that introducing of the donating amino-group in the aromatic ring increases the HOMO energy, just as it was expected. Noteworthy, that chlorine and bromine atoms, which are also ortho-substituents, decrease greatly the HOMO energy, making such compounds less effective. This is the result of their strong negative inductive effect. However, we

expected that their positive resonance effect plays more considerable role in increasing of electron density in the aromatic ring. Thiocyano-group was also expected to be slightly electron-donating, but it reveals quite strong withdrawing effect, just a little lower than that of nitro-group. Localization of molecular orbitals also confirms this fact, as HOMO in thiocyanobenzotriazole **6** is placed on the atoms of the functional group, similar to the compound **2**, and opposite to the **1** and **3-5**, where HOMO is localized in aromatic ring (figure 3).

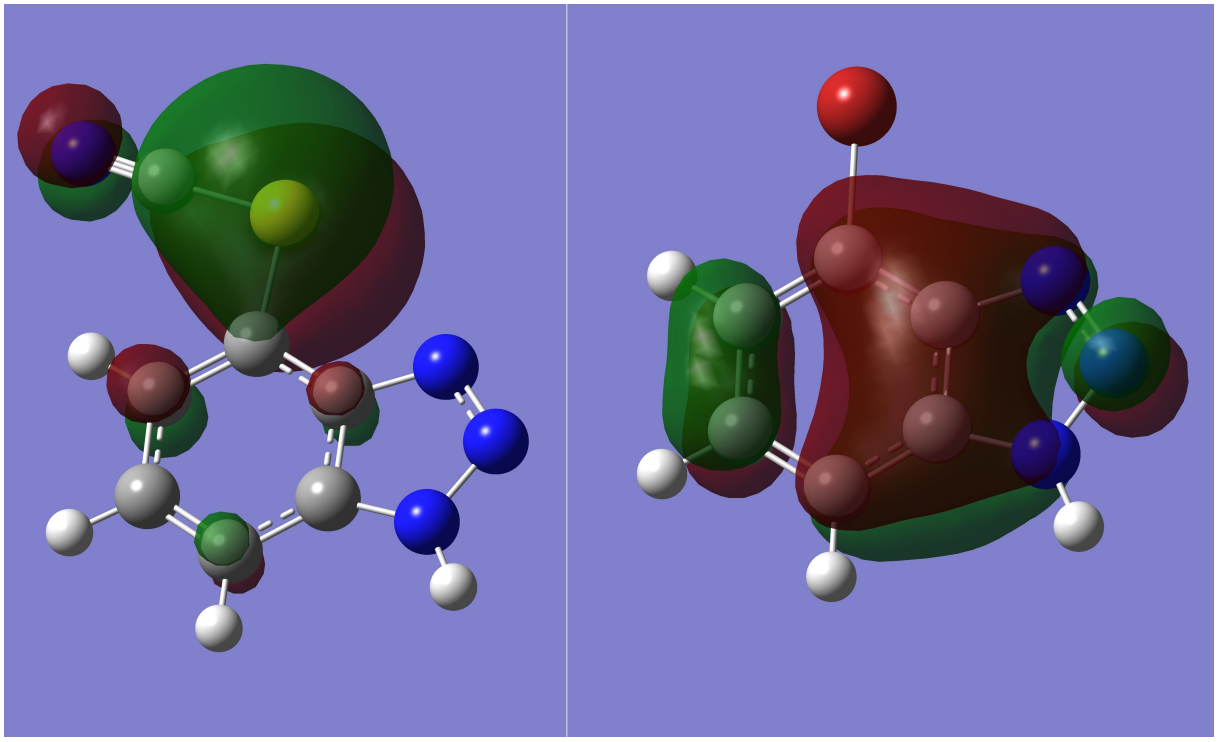

Figure 3. HOMO localization in compounds **6** and **4**, respectively.

These results show us, that this work should be continued, because the synthesized compounds (except **3**) demonstrate poor electronic properties, which are even worse that that of benzotriazole itself. However, benzotriazoles with electron-donating groups, such as amine-, hydroxy-, alkoxy- and others, should reveal strong anticorrosive activity and may be used in industry due to their low toxicity and simplicity of their preparation.

5. Conclusion

In this study we suggested the method for synthesis of C-substituted benzotriazoles from benzotriazole itself by diazotation reaction. It allows to prepare the wide range of benzotriazole derivatives from commercially available reagents in mild conditions. Some of these compounds can be used as effective corrosive inhibitors. Quantum-chemical evaluation of electronic properties of the target compounds were performed, revealing significant electron-withdrawing effect of halogen atoms and thiocyano-group.

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