

Some Aspects of Chemical Transformations of Trinitrotoluene

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Abstract - Some new aspects of chemical transformations of trinitrotoluene into products of civil needs are reviewed. The new approach to a cheap and ecological way of chemical modification of nitro aromatic compounds into non explosive products are described. Basing on the proposed reactions, some new hydroxyimino and azo compounds and their metal complexes were synthesized and described by spectroscopic and theoretical methods. Their possible ways of application are proposed.

Keywords – azo- and hydroxyimino compounds, methylphloroglucinol, synthesis, applications

I. INTRODUCTION

Among various technogenic environmental problems, the recycling of explosives removed from ammunition of arms is of a great significance in now days. Blasting or burning methods of utilization are rejected by civilized countries as ecologically and economically barbarous. Major residue of ammunition manufactured until 1960-1970 are 2,4,6-trinitrotoluene (TNT) and 1,3,5-trinitrobenzene (TNB) as a product of an oxidative demethylation of TNT.

As the technology of extraction of TNT from ammunition is effectively developed, the problem of edition of effective, ecologically and economically expedient technology of its transformation into chemical products of civil appointment is of a great significance.

In order to find new civil applications of products of transformation of TNT, new amino-, hydroxyimino- and azo compounds and their metal complexes were synthesized and investigated by a set of spectroscopic and theoretical methods.

In nowadays, 4 million tons of the ammunition, which is the subject to utilization, is accumulated on our Planet,

and 350 thousand tons from them make the explosives (basically trinitrotoluene, TNT). Destruction of the ammunition is regarded as damage at least for two reasons. First, the results of the substantiated work of various sectors of society (scientists, engineers, designers, workers, testers) represent irrevocable losses, which lower and worsen welfare of big groups of the population of the countries and society as a whole. Second, the negative influence of the destruction of the ammunition is connected with violation (deterioration) of ecology of the environment, pollution of the soil, superficial (rivers, lakes, seas) and underground waters, vegetation and air pollution.

The transformation of explosive trinitrotoluene into non-explosive products is based upon reduction of highly energetic nitro-groups into ecologically safe amino-groups and/or their substitution by hydroxy-groups.

2,4,6-Trihydroxytoluene (methylphloroglucinol, MPG) possesses strong and attractive synthetic potential because of its specific structure. Unfortunately, until the last decade it practically has not been realized because of small yields of its isolation and, as a result, of its high cost. The possible ways of transformation of TNT into MPG are presented on the **Fig. 1**.

Recently, the economically efficient method of isolation of MPG on base of 2,4,6-trinitrotoluene [7,8] was developed. The one pot reaction proceeds in acidic boiling aqueous media in presence of ammonium containing catalysts. The advantages of this method are high yields (more than 75%); high purity of the product (95 – 98% by NMR); possibility to use concentrated solutions; significantly decreased time of the reaction. In addition, it allows avoid corrosion by replacement of chlorides by sulfates, fluorides or other salts.

As the eco-friendly methods of transformation of the technogenic wastes into products of civil needs are required [9], the new aspects of the further chemical transformation of MPG was studied.

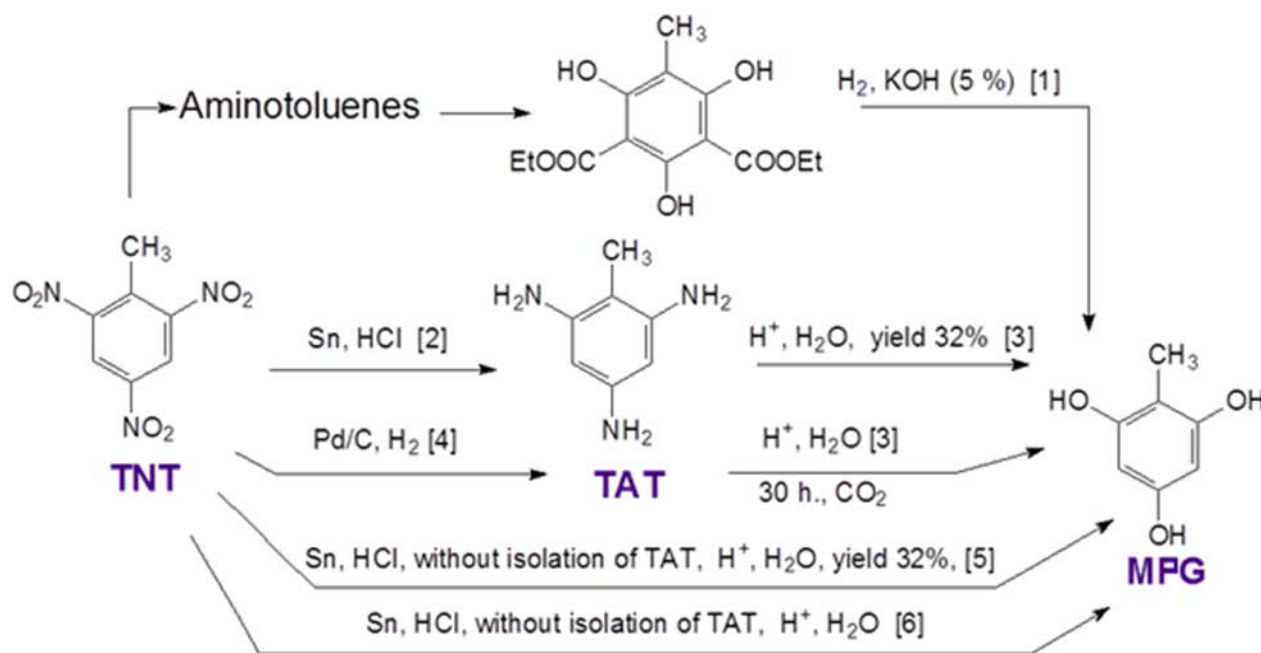


Fig. 1. Methods of transformation of TNT into MPG.

II. RESULTS AND DISCUSSION

A. Transformation of MPG into azo dyes and azo pigments.

As a result of our studies, the methods of synthesis of mono- and diazo-compounds derived from MPG with high yields (70-90 %) were elaborated, and more than 100 new azo-compounds were isolated [10, 11]. All the obtained substances were tasted as acid and disperse dyes for wool, polycapromamide and polyester fibres. Majority of them showed good coloristic characteristics with the intensive colors from yellow to blue depending upon substituent in the aryl-radical.

It was shown that presence of MPG-fragments in the composition of azo dyes increases their resistance to physical and chemical treatments. Some of them possess high thermo stabilities (m.p. 230 – 360 °C) and may be used for dyeing of polymers and wood.

The addition of NaOH to the solutions of azo-derivatives of MPG provokes two stepwise equilibrium processes. In the pH interval 6.5 – 8.0 in the electronic absorption spectra (Figure 2), the long-wave band undergoes bathochrome shift to 471.0 nm ($\log \epsilon$ 4.32), and the short-wave band appears at 264.4 nm ($\log \epsilon$ 3.70). The further addition of NaOH leads to a strong bathochrome shift of both two bands: 533.3 nm ($\log \epsilon$ 4.12) and 382.2 nm ($\log \epsilon$ 3.69). This change in the spectrum is explained by the transformation of the substance into hydrazo-form with its further dissociation.

The change in color from red to violet in the pH range 8 – 8.5 allows proposing the azo-derivatives of MPG as acid-base indicators.

The calculated pK_a values of the MPG azo derivatives were found as (10.16 – 8.50) \pm 0.79. This is in

a good accordance with the literal data on the acidities of azo-derivatives of MPG and other polyphenols.

The addition of the solutions of metal salts to the solutions of the described azo dyes provokes the same changes in the UV-VIS spectra as ionization of the compounds, i.e. bathochromic shift of the long wave band (Fig. 2). This correlates with the behavior of traditional azo dyes. The evaporation of solutions provokes formation of varnish-like films of intense colors. The structure of metal complexes was concluded by the correlation of spectral data of the compounds and the theoretical modeling (Fig. 3) [13].

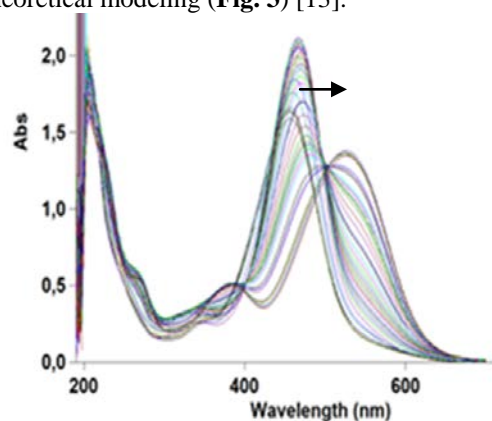
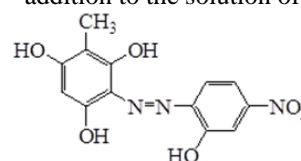


Fig. 2. Changes in UV-VIS spectra at stepwise NaOH addition to the solution of



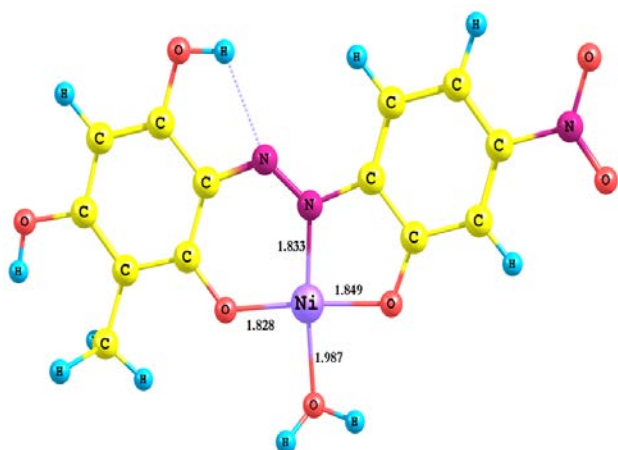


Fig. 3. Geometry optimization of the NiL·H₂O complex (DFT/B3LYP),

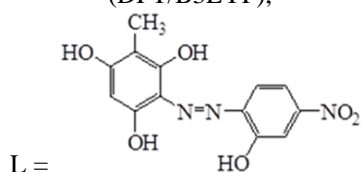


Fig. 4. The potentiometric titration curve of the aqueous solution of the neutral dihydroxyimino-MPG with NaOH.

Addition of the dihydroxyimino-MPG aqueous solutions to the solutions containing cations of heavy metals (Cr^{3+} , Fe^{2+} , Fe^{3+} , Co^{2+} , Ni^{2+} , Cu^{2+} , Zn^{2+} , Cd^{2+} , Ba^{2+} , Pb^{2+}) which are reported as urban and industrial pollutants of natural waters and soils [14, 15] provoked rapid and practically full precipitation of complex compounds. The X-Ray analysis indicated that the organic monoanions act as bidentate chelating ligands, coordinating the metal cations through an N atom of the non-deprotonated hydroxyimino group and an O atom of the neighboring oxo group (**Fig. 5**) [16].

The in vitro tests showed high fungicide activity of the azo dyes derived from MPG and their metal complexes (*Aspergillus niger*, *Aspergillus flavus*, *Penicillium chrysogenum*, *Ulocladium atrum*, *Chaetomium globosum*). The above-mentioned micromycetes are often present on textile materials and cause both mechanical and chemical destruction of fibers. The performed tests showed that the majority of the samples have an overwhelming effect on the development of test cultures, and some of them completely suppress growth or sporulation.

The correlation between the complex formation and fungicide ability of the substances was established for variety of samples.

B. Hydroxyimino-derivatives of MPG.

As it was shown by the X-Ray Single Crystal analysis, the reaction of nitrosation of MPG leads to formation of the anionic form of a triketohydroxyimino tautomer:

Dark-red plates of single crystals of the only product of MPG nitrosation in the form of the sodium salt were obtained by recrystallization from ethanolic aqueous solution. Their treatment by a strong mineral acid leads to the precipitation of the neutral form of the organic molecule which electronic spectrum coincides with that of the sodium salt. This fact indicates rather strong acidic properties of the substance. The potentiometric titration curve of the neutral dihydroxyimino-MPG with NaOH (**Fig. 4**) is assigned to the existence of two dissociation processes. One proton seems to dissociate in the 4 - 7 pH interval. The $\text{pH}_{1/2}$ value is 5.6 ± 0.1 which correlates with the dissociation constant of benzoic acid ($K_a = 6.5 \cdot 10^{-5}$).

The dissociation of the two oxime protons occurs at once in the pH interval from 7.0 to 9.5 ($\text{pH}_{1/2} 8.15 \pm 0.12$). The pK_a value correlates with that of aromatic oximes.

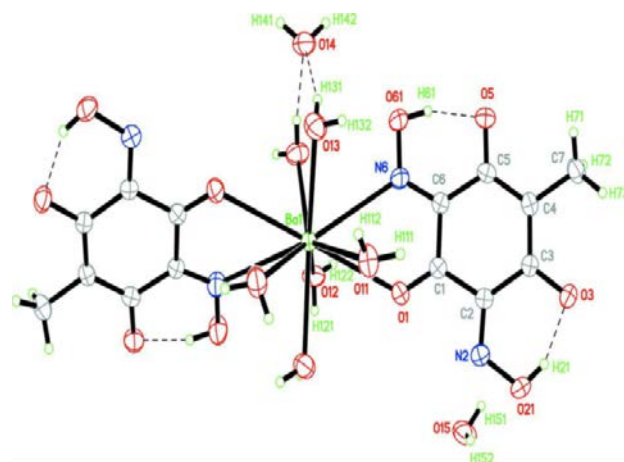


Fig. 5. Molecular structure of the Ba complex of the dihydroxyimino-MPG.

Low solubility of the dihydroxyimino-MPG metal complexes and significant shift of the ligand absorption bands in the electronic spectra (**Fig. 6**) allows to propose the organic species as analytical reagents and extractors of ions of heavy metals from the waste waters.

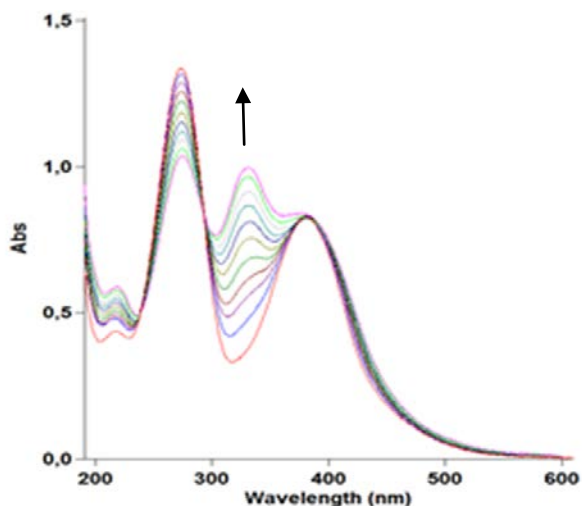


Fig. 6. Change in UV-VIS spectra of the dihydroxyimino derivative of MPG at stepwise addition of NiCl_2 .

C. Compounds containing both azo and hydroxyimino groups.

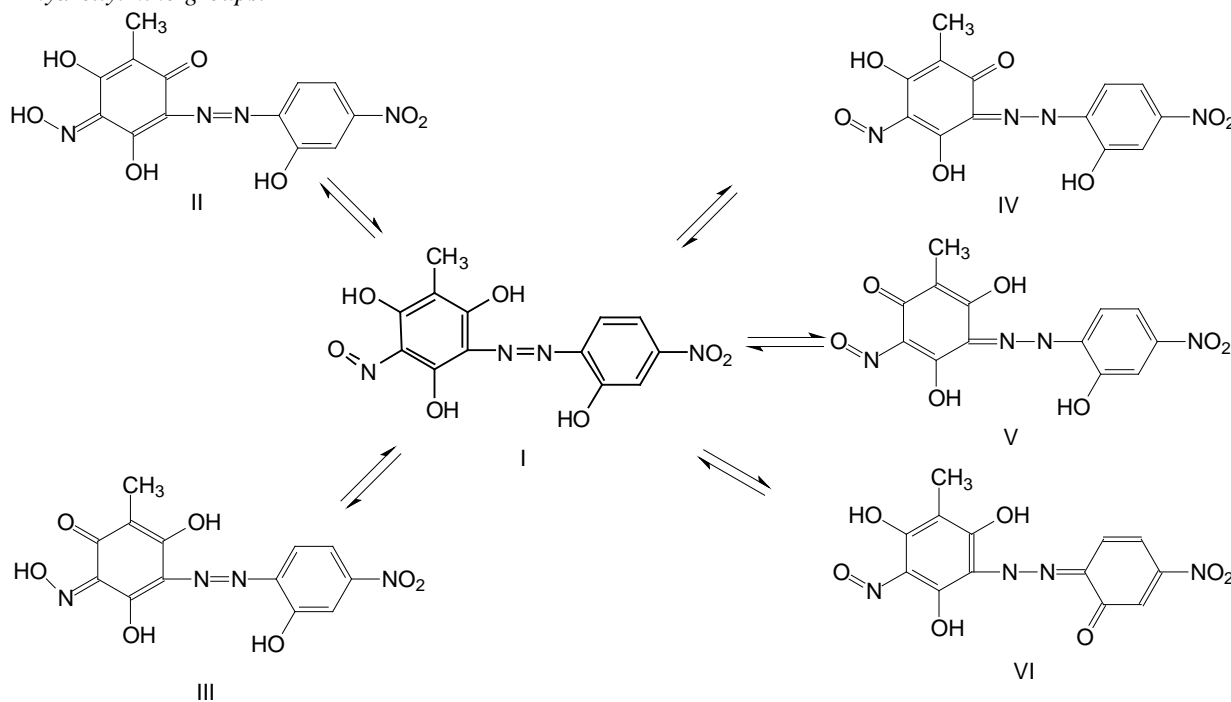


Fig. 7. Some possible tautomeric forms for azo-hydroxyimino derivatives of MPG.

As it was shown in the previous sections, hydroxyazo derivatives of MPG possess properties of dyes and pigments which coloring characteristics strongly depend on the ability of their complexation with metals [17]. The hydroxyimino-derivatives of MPG are good reagents for extraction of heavy metals from the environment. Unfortunately, the organic species do not possess adhesive properties and cannot be fixed on fibers. In order to combine both the coloristic and extracting properties, the nitrosation of mono-azo MPG dyes was performed. The introduction of several electron donating fragments in the benzene ring leads to the multiplicity of the ionic and tautomeric equilibria as well as coordination modes in reactions of complex formation (**Fig. 7**). To describe the properties of the compounds, it is necessary to detect the dominant forms of the organic species.

The addition of alkalis or solutions of transition metals salts to the solutions of the hydroxyimino-azo derivatives of MPG provokes the same type of the change in the UV-VIS absorption spectra as for the dihydroxyimino-compounds (**Fig. 8**).

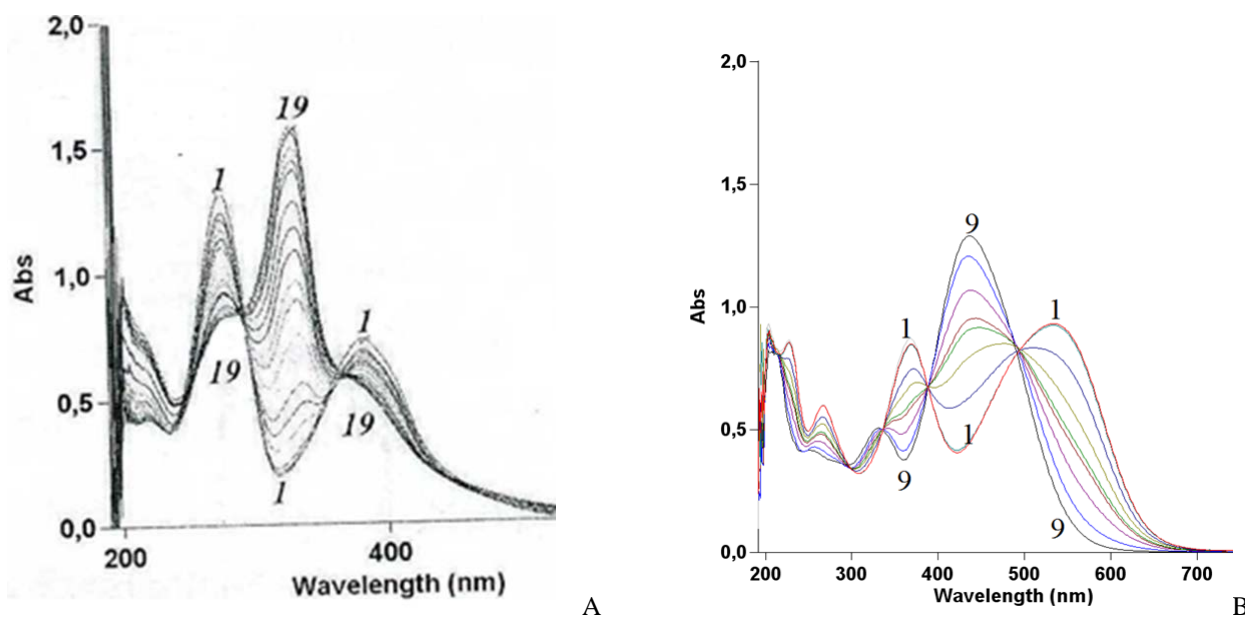
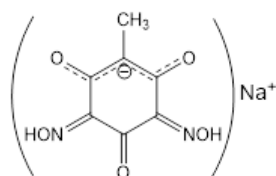
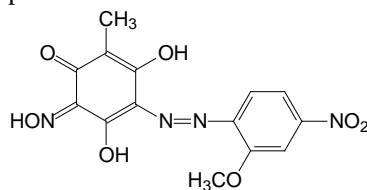


Fig. 8. Changes in the UV-VIS spectra at stepwise addition of NaOH to the solutions of



(A)

and



(B).

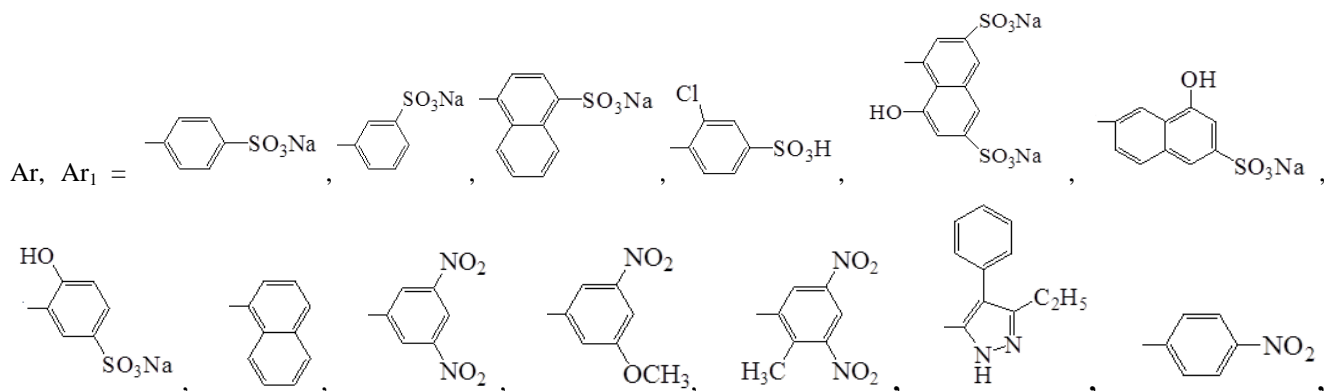
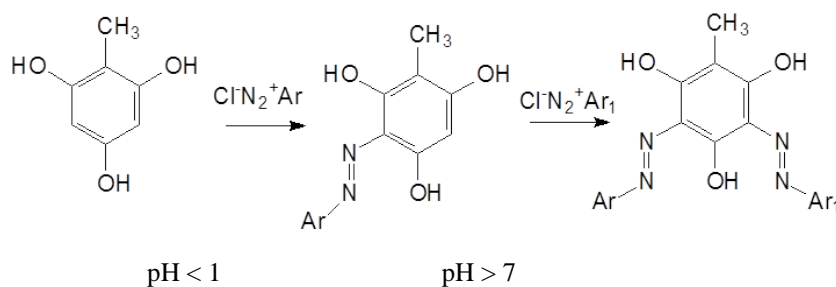
This indicates that the substances exist in the solutions in the forms of azo-hydroxyimino tautomers II and III (Fig. 7). The ability of the tautomer III to be stabilized by an intramolecular H-bond between the neighboring =NOH and C=O groups makes it more preferable. The ionization process involves nitroso-group better than hydroxy-groups [18].

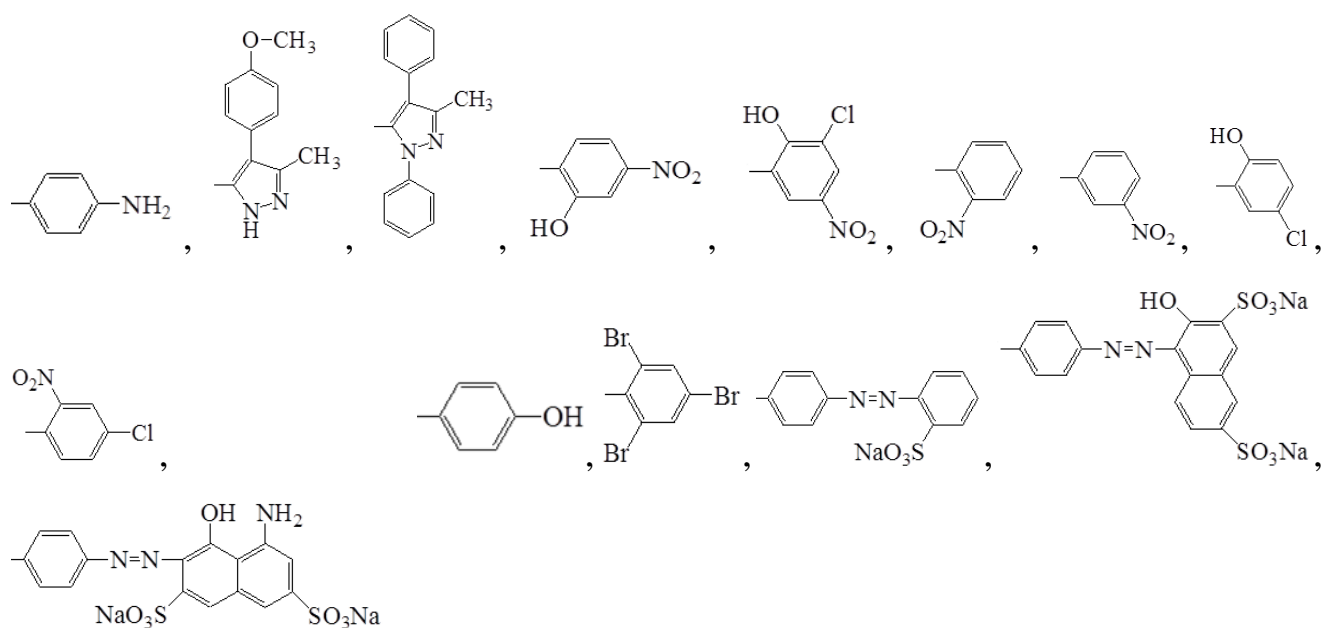
The introduction of hydroxyimino groups to the composition of azo dyes derived from MPG increase their

anti-fungal activity and formation constants of their metal complexes.

III. EXPERIMENTAL.

The azo-coupling of MPG with a large variety of diazonium salts was studied in the temperature interval $0 \div 5^\circ\text{C}$, in the pH range from 1 to 12 according to the following reaction:

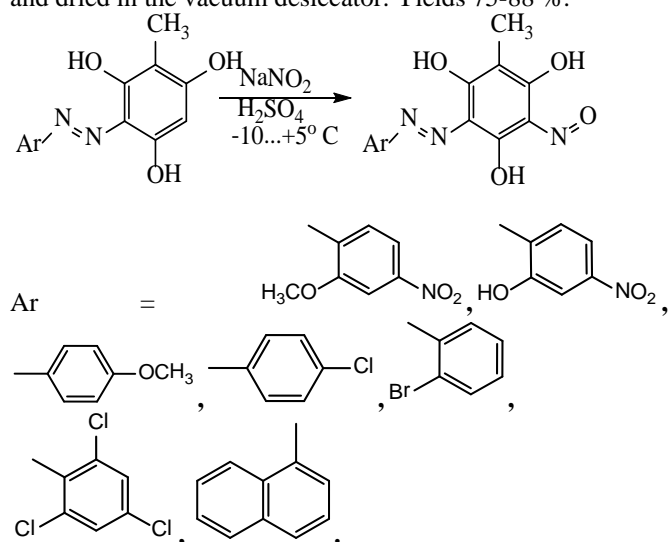




In total, more than 100 compounds were isolated according to the methods described in [10, 11].

The dihydroxyimino-derivative of MPG was isolated within the reaction of nitrosation. The structure was proved by X-Ray single crystal analysis, and the method of synthesis is presented in [12].

The nitrosation of mono azo-derivatives of MPG was performed by mixing of its ethanol solutions with the NaNO_2 aqueous solution in the mole ratio 1 : 1. Then the reactional mixture was cooled to -10°C , and 50% H_2SO_4 was drop wise added in the proportion of 1 : 0.5 (the temperature of the solution should not exceed $+5^\circ\text{C}$). The formed nitroso-derivative precipitates were filtered off and dried in the vacuum desiccator. Yields 75-88 %.



The substances were recrystallized from ethanol and characterized by the elemental analysis, MS, IR, ^1H and ^{13}C NMR spectroscopy.

The UV-VIS spectroscopic titrations were performed on the Cary-50 spectrophotometer in ethanol solutions in the wave lengths interval 200 – 700 nm.

The quantum chemical calculations were performed by the DFT B3LYP method.

IV. CONCLUSION

The proposed chemical ways of transformation of the explosive TNT wastes into the products of civil needs (azo-dyes and azo-pigments with high resistance to physical and chemical treatments and fungicide activity, as well as analytical reagents and extractors of ions of heavy metals from the waste waters) are attractive from the ecological and economical points of view. They do not demand expensive reactants, concentrated aggressive media and high temperatures. They aim to prevent the environmental pollution by technogenic wastes. They allow obtaining new materials and compounds with a set of useful properties. At least, finding a way of converting TNT into civil products would allow the TNT production facilities to be kept up.

Methylphloroglucinol as a possible product of successive TNT conversion is can be used as the starting compound in the production of heat-resistant thermosetting resins; as a component of heat-resistant dips and insulation for electromotors, generators, and transformers; as a component of polyisocyanate compositions with a high polymerization rate; in the fabrication of photosensitive and lithographic plates; in the synthesis of antibacterial and antiviral drugs with a flavone or xanthone structure; etc. However, until now because of its low availability and

expensiveness, MPG has not been considered as the starting compound for the above applications.

The technology suggested in the above paper provides a solution to the problem of utilizing expired ammunition in an environmentally friendly and economically efficient way.

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