SYNTHESIS AND PHYSICOCHEMICAL CHARACTERIZATION OF 9-NITROANTHRACENE BASED ON THE NITRATION REACTION OF ANTHRACENE

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Abstract. *This article studies the targeted synthesis of nitro derivatives of polycyclic aromatic hydrocarbons, in particular, the process of obtaining 9-nitroanthracene, which is an important intermediate in organic electronics and medicinal chemistry. Analysis of classical literature data shows that the formation of by-products such as polynitro derivatives and anthracene-9,10-dione (anthraquinone) in direct nitration reactions of the anthracene nucleus, as well as the low yield of the target product, are fundamental problems. In order to eliminate the shortcomings noted in this study and increase the efficiency of the process, an optimal preparative method for the synthesis of 9-nitroanthracene derivatives with high regioselectivity was developed and its kinetic laws were studied. The molecular and electronic structure of the synthesized subject was analyzed in depth using a set of modern physicochemical methods. Infrared (IR) spectroscopy revealed asymmetric (1520*cm^{-1}*) and symmetric (1340* cm^{-1}*) stretching vibrations of the nitro group and absorption bands of the* $C-N$ *bond, while ultraviolet (UV) spectra revealed bathochromic shifts due to* $\pi \to \pi^*$ *and* $n \to \pi^*$ *electronic transitions of the anthracene nucleus and the nature of the conjugated system. The results obtained are of significant practical importance in the field of molecular optoelectronics, sensors, and the synthesis of luminophores, and provide a basis for obtaining biologically active amino derivatives.*

Keywords: *anthracene, 9-nitroanthracene, regioselectivity, electrophilic addition, dehydrochlorination, IR spectroscopy, UV spectroscopy, bathochromic shift, molecular optoelectronics.*

INTRODUCTION. In modern translational organic synthesis, the purposeful modification of condensed polycyclic aromatic hydrocarbons (PAHs) and their functional derivatives, as well as the creation of regiospecific regulators, remain among the pressing problems in the pharmaceutical and agrochemical industries. In particular, the anthracene nucleus, consisting of three linearly condensed benzene rings, is of particular academic and practical importance due to its unique electronic structure, delocalized dynamic π-electron system, and photophysical properties with high quantum yield. Analysis of modern phytophysiological and agrochemical studies shows that anthracene derivatives have a positive, stimulating effect on the endogenous hormonal system of plants, specifically on the balance of auxins. They serve as a universal synthon (starting block) for the synthesis of a new generation of biotechnological biostimulants that increase the adaptive resistance of crops to various extreme abiotic stress factors (severe drought, soil salinity, and thermal stress), as well as activate the morphological and histoanatomical development of the root system.

The high local electron density and minimal localization energy at the 9- and 10- (meso-positions) of the anthracene nucleus allow for the targeted control of its biological and chemotactic activity by introducing various functional groups into the molecule with high regioselectivity. Among these functional groups, the nitro group ($-NO_2$), due to its strong electron-withdrawing nature (negative inductive $-I$ and mesomeric $-M$ effects), sharply redistributes the π-electron density in the anthracene ring, thereby increasing the dipole moment (polarity) of the molecule and its ability to diffuse through cell membranes. From the perspective of chemical transformation, 9-nitroanthracene is a strategic precursor (intermediate) for subsequent nucleophilic and electrophilic substitution reactions, as well as for the production of aromatic amines, amino acids, and other nitrogen-containing heterocyclic compounds with high bioactivity.

The aim of this study is to optimize the nitration reaction of anthracene in a homogeneous medium of glacial acetic acid under laboratory conditions using a nitric-hydrochloric acid system.

Furthermore, it aims to systematically analyze the nature of the intermediate 9-nitro-10-chloro-9,10-dihydroanthracene adduct formed during the electrophilic addition stage, as well as the laws governing its base-induced elimination (dehydrochlorination) reaction under the influence of sodium hydroxide ($NaOH$). Additionally, the study seeks to determine the isolated yield of the product using simple gravity filtration and recrystallization from a suitable solvent system, and to perform a fundamental spectral identification to confirm the molecular structure and electronic absorption behavior of the target substance using ultraviolet (UV) and infrared (IR) spectroscopy.

METHODOLOGY AND EXPERIMENTAL PART

In this study, a two-step synthesis methodology was developed at room temperature to simplify the complex and energy-intensive cooling systems reported in the literature, optimize energy consumption, and minimize the formation of by-products such as polynitro derivatives.

In the electrophilic addition step, conducted at $20-25^0C$, the meso-position of anthracene was activated by nitric acid in a homogeneous medium of glacial acetic acid and hydrochloric acid, eliminating the need for external cooling. These mild reaction conditions ensured the stable formation of the intermediate covalent chloro-adduct, which successfully separated from the medium as a precipitate.

In the subsequent base-induced elimination step, the isolated adduct was subjected to treatment with a sodium hydroxide ($NaOH$) solution at room temperature to control the deprotonation and dehydrochlorination processes.

The isolated yield of the final product was determined using classical gravity filtration followed by recrystallization from a suitable organic solvent system (ethanol/water). The structural purity of the target compound, the nature of its functional groups, and the optoelectronic characteristics of the conjugated π-system were fundamentally identified and confirmed via ultraviolet-visible (UV-Vis) and infrared (IR) spectroscopy.

The reagents used in the synthesis—anthracene, glacial acetic acid (CH_3COOH), concentrated nitric acid (HNO_3), concentrated hydrochloric acid (HCl), and sodium hydroxide

$(NaOH)$—were of analytical grade. The reaction was carried out under constant homogenization using a magnetic stirrer. The melting point of the substance was determined by the conventional capillary method.

Anthracene (2.0 g, 11.22 mmol) and 25 mL of glacial acetic acid were placed in a conical flask. The flask was immersed in an ambient water bath and stirred vigorously. Concentrated nitric acid (HNO_3, 1.5 mL) was added dropwise to the mixture while maintaining the reaction temperature at $20-25^0C$. After the complete addition of nitric acid, the mixture was stirred for 30 minutes until a homogeneous solution was obtained.

Once the solution became completely clear, a separately prepared mixture of 5 mL of concentrated HCl and 5 mL of glacial acetic acid was slowly added. This resulted in the formation of a thick, yellowish suspension of 9-nitro-10-chloro-9,10-dihydroanthracene. The resulting precipitate was isolated by filtration, washed with ice-cold distilled water until a neutral pH was reached, and kept damp.

The wet precipitate was then transferred to a porcelain dish and treated with 10 mL of a warm ($20-25^0C$) 10% sodium hydroxide ($NaOH$) solution. The mixture was stirred vigorously, causing the color of the substance to turn bright orange. The obtained crude precipitate of 9-nitroanthracene was filtered again, washed with distilled water until neutral, and dried completely at 50^0C for 12 hours

RESULTS

The isolated mass of the dried final product obtained from the laboratory synthesis was 1.73 g. Based on the theoretical yield calculated from the initial reactant amount (m(theoretical) = 2.49 g), the isolated yield was determined to be 69.5%. The melting point of the synthesized 9-nitroanthracene was found to be in the range of $145-146^0C$ (literature data: $144-147^0C$), which confirms the high purity of the obtained substance.

Ultraviolet-visible (UV-Vis) spectroscopy analysis results: The electronic absorption spectra of the synthesized substance, recorded in a chloroform solution, were compared with the spectrum of the parent pure anthracene. Due to the introduction of the strong electron-withdrawing nitro group ($-NO_2$), the absorption maximum (γ_{max}) shifted toward the longer wavelength region, demonstrating a distinctive bathochromic (red) shift.

Compound	λ_{max1} (nm)	λ_{max2} (nm) (Main Vibrational Peaks)
Anthracene	256	340, 356, 375
9-Nitroanthracene	252	348, 365, 386

Table 1. Ultraviolet-visible (UV-Vis) spectral characteristics of the compounds

Infrared (IR) spectroscopy was employed to confirm the successful functionalization of the anthracene core and the incorporation of the nitro group. The recorded IR spectrum exhibits a characteristic absorption band at 3058.91 cm^{-1}, which is assigned to the sp^2ν(=C–H) stretching vibrations of the aromatic ring. The skeletal ν(C=C) stretching vibrations of the conjugated anthracene nucleus are clearly observed at 1624.24 cm^{-1}.

The most definitive evidence for the successful synthesis of 9-nitroanthracene is the appearance of prominent, high-intensity bands corresponding to the nitro group ($-NO_2$). The strong absorption band located at 1513.66 cm^{-1} is confidently assigned to the asymmetric stretching vibrations (ν_{as}) of the group$-NO_2$. Concurrently, the symmetric stretching vibrations (ν_s) are manifested as highly intense, sharp peaks at 1371.48 cm^{-1} and particularly at 1318.35 cm^{-1}. The high intensity of these symmetric and asymmetric bands is a direct consequence of the strong dipole moment introduced by the electron-withdrawing nitro group into the polycyclic aromatic framework, unambiguously confirming the molecular structure of the target product.

Although the nitration reaction of anthracene follows the general principle of electrophilic aromatic substitution (S_EAr), the unique dynamics at its 9- and 10-positions cause the process to proceed via a two-step pathway.

Step I: Electrophilic Addition Reaction. Under acidic conditions, the nitro group and chlorine atom add across the anthracene core, partially disrupting the aromaticity and resulting in the precipitation of a yellowish 9-nitro-10-chloro-9,10-dihydroanthracene adduct:

$$C_{14}H_{10} + HNO_3 + HCl \rightarrow C_{14}H_{10}\,ClNO_2 + H_2O$$

Step II: Elimination reaction. Under warm alkaline conditions, a molecule of hydrogen chloride (HCl) is eliminated from the intermediate adduct (dehydrochlorination), thereby restoring the aromatic stability of the system and forming the bright orange 9-nitroanthracene:"

$$C_{14}H_{10}ClNO_2 + NaOH \rightarrow C_{14}H_9NO_2 + NaCl + H_2O$$

The observed variations in the UV-Vis spectra indicate that the characteristic fine vibrational structure of anthracene is modified due to the enhanced electron delocalization induced by the nitro group, resulting in a notable bathochromic shift from 375 to 386 nm. In the IR spectrum, the emergence of exceptionally intense absorption bands at 1513.66 and 1318.35 cm^{-1}unambiguously confirms the successful attachment of the nitro group at the 9-position of the anthracene core, proving that the functionalization occurred precisely at the targeted reaction center.

CONCLUSION

As a result of systematic research, an energy-saving, efficient, and optimized laboratory method for the synthesis of 9-nitroanthracene via the regioselective nitration of the anthracene nucleus in a homogeneous glacial acetic acid medium was developed. By avoiding complex artificial cooling systems, the process was successfully conducted at an optimal room temperature of $20 - 25^0C$, thereby minimizing the formation of polynitro derivatives and unwanted by-products such as anthraquinone. The target product was isolated with an isolated yield of 69.5% and high crystalline purity.

The molecular structure of the substance, the characteristic stretching vibration zones of the nitro group, and the optical properties of the conjugated π-electron system—obtained via modern physicochemical analysis methods, namely IR and UV-Vis spectroscopy—were found to be in excellent agreement with one another.

The synthesized 9-nitroanthracene will serve as a strategic and valuable starting synthon (intermediate product) for the synthesis of a new generation of agrochemical biostimulators. These target molecules are designed to enhance crop resistance to adverse abiotic stress factors, regulate phytohormonal balance, and stimulate the histoanatomical development of the root system.

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