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NAPHTHYLAMINE AND ITS DERIVATIVES

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Abstract: This research paper explores the chemical compound naphthylamine, a primary derivative of naphthalene, along with its structural isomers and numerous applications across the chemical industry. Naphthylamine, being a primary aromatic amine, exhibits high reactivity and is widely used as a precursor in the synthesis of dyes, pharmaceuticals, rubber additives, and various organic intermediates. The study focuses on both isomers of naphthylamine—1-naphthylamine (α-naphthylamine) and 2-naphthylamine (β-naphthylamine)—emphasizing their structural differences and functional significance. Special attention is given to the synthesis techniques of these compounds, including the Bucherer reaction and catalytic reduction of nitro derivatives. Additionally, the paper highlights the importance of chromatographic analysis (TLC) and spectrometry in identifying synthesized products. One of the key concerns addressed in this work is the carcinogenic nature of 2-naphthylamine, which poses significant health risks upon exposure. Therefore, proper handling, storage, and industrial safety protocols are essential. The results of experimental synthesis of novel naphthylamine-based compounds further demonstrate their potential application in advanced chemical manufacturing. This work contributes to the broader understanding of aromatic amine chemistry and underlines the industrial and environmental relevance of naphthylamine and its derivatives.

Keywords: aniline, synthesis, compound, derivative, process, naphthylamine, chromatography, amine.

Relevance: Naphthylamine and its derivatives are classified as highly toxic compounds. Notably, aniline and 1-naphthylamine are considered priority environmental pollutants due to their potential to cause significant harm to air and water quality. Their maximum permissible concentrations (MPCs) are strictly regulated. The release of these substances into the environment is associated with various technological processes and industrial incidents, including the discharge of chemical waste, the breakdown of pesticides, and emissions from motor vehicles. Therefore, the study of the physicochemical properties, synthesis methods, and potential applications of naphthylamine derivatives is of high scientific and environmental significance. Due to their high toxicity, compounds such as aniline and 1-naphthylamine are classified as priority environmental pollutants. They have established maximum permissible concentrations (MPCs) in air and water, which are strictly regulated. Their emission into the atmosphere and environment is often a consequence of technological processes and industrial accidents, including chemical waste disposal, pesticide degradation, and emissions from motor vehicles. The primary aim of this article is to explore the organic compound naphthylamine, a key derivative of naphthalene, by investigating its derivatives, properties, and synthesis through various pathways.

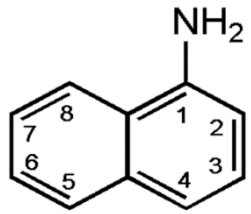
The objective of the study is to examine the structure, reactivity, and formation mechanisms of naphthylamine derivatives, to define the optimal reaction conditions for their synthesis, and to identify their chemical properties. Newly synthesized naphthylamine derivatives will be analyzed using spectrometric methods to determine their applicability across industries. These compounds, which involve the incorporation of amine groups (-NH_2) and other functional groups into the naphthalene ring, belong to an important class of organic compounds. They are extensively used in the chemical industry, particularly in the synthesis of dyes, pharmaceuticals, rubber materials, and other critical substances. The properties and applications of these derivatives are significantly

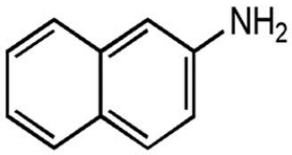
influenced by their molecular structure, the nature of their functional groups, and their positional orientation within the aromatic ring.

Objectives:

- Investigate the structure and reactivity of naphthylamine derivatives.
- Analyze their formation mechanisms and determine reaction conditions.
- Synthesize new naphthylamine derivatives and evaluate their application potential using spectrometric methods.

Materials and Methods: Naphthylamines are organic compounds classified as derivatives of naphthalene, characterized by the general molecular formula $C_{10}H_7–NH_2$. They belong to the group of primary aromatic amines and possess a molecular weight of 143.18 g/mol. These compounds exist in isomeric forms and serve as fundamental building blocks in the synthesis of various industrial and pharmaceutical substances.





1-naphthylamine (α-naphthylamine) 2- naphthylamine

Synthesis and Properties

Synthesis:α-Naphthylamine was first synthesized by N.N. Zinin via the reduction of 1-nitronaphthalene with ammonium sulfide, a method now referred to as the Zinin reaction. Additionally, 1-nitronaphthalene can be reduced in an acidic medium using iron or zinc as reducing agents. Another method involves the heating of α-naphthol with ammonia in the presence of a zinc chloride complex to yield α-naphthylamine.

2-Naphthylamine (β-naphthylamine) is typically obtained from β-naphthol through the Bucherer reaction, which involves heating with ammonium sulfite and aqueous ammonia under pressure.

Naphthylamines can also be synthesized by heating the corresponding naphthoic acids with hydroxylamine and polyphosphoric acid. The reduction of nitronaphthalene in acidic medium with iron or zinc is also an effective approach for obtaining naphthylamines.

Physical Properties

Naphthylamines are colorless crystalline solids that gradually darken when exposed to air. They are freely soluble in ethanol and diethyl ether, sparingly soluble in water, and can sublime with steam distillation.

Chemical Properties

Naphthylamines exhibit the typical reactivity of aromatic amines. In strong inorganic acids, they form stable ammonium salts as follows:

$$C_{10}H_7—NH_2 + H^+ \rightarrow C_{10}H_7—NH_3^+ \quad (1)$$

Acylated by organic acids:

$$C_{10}H_7—NH_2 + CH_3—COOH \rightarrow C_{10}H_7—NH—CO—CH_3 \quad (2)$$

When heated to 180°C in alkaline or acidic solutions (and up to 400°C in aqueous solutions), naphthylamines undergo transformation into the corresponding naphthols.Naphthylamines and naphthylamine sulfonic acids are of great importance in the production of azo dyes, serving as diazo compounds and coupling agents. Moreover, di- and tri-sulfonic acids of naphthylamine are used as

intermediate products in the synthesis of amino-naphthol sulfonic acids, which are formed by replacing sulfo groups with oxy groups through alkaline fusion.Naphthylamine is considered an analogue of aniline and represents a class of primary aromatic amines structurally related to naphthalene and naphthol. It exists in two isomeric forms, α- and β-naphthylamine, designated by Greek letters based on the position of the amino group on the naphthalene ring. In recent years, naphthylamine has gained significant relevance in dye chemistry due to its role in the synthesis of various azo dyes derived from the naphthalene structure (see synthetic organic dyes).One of the key synthetic routes to naphthylamine involves the reduction of nitronaphthalenes using ammonium sulfide (Zinin reaction), iron with acetic acid, or iron with hydrochloric acid, according to the following general equation:

$$C_{10}H_7NO_2 + 3H_2 = C\ 10H_7NH_2 + 2H_2O \quad (3)$$

From naphthol:

Naphthylamine can also be synthesized from naphthol by treating it with ammonia under pressure at a temperature of 150–160°C, according to the following reaction:

$$C_{10}H_7OH + NH_3 \rightarrow C_{10}H_7NH_2 + H_2O \quad (4)$$

When heated with $ZnCl_2$ in sealed vessels at elevated temperatures, naphthylamine can be obtained through various synthetic routes. For example, heating in the presence of $2NH_3$ (according to Merz and Weith), or $CaCl_2 \cdot 2NH_3$ (according to Bamberger and Benda), or through the use of ammonia solution (ammonium hydroxide) together with sodium acetate and crystalline acetic acid. In the latter case, the direct product of the reaction is acetonaphthalide.In all three of these synthetic methods, the formation of a small amount of dinaphthyl amines as by-products is common. These approaches are typically applied for industrial-scale production of β-naphthylamine, whereas α-naphthylamine is more commonly synthesized by reducing α-nitronaphthalene. Specifically, synthetic α-naphthylamine can be obtained by heating a mixture of pyrolignic acid and aniline with zinc chloride at 300°C, according to the following reaction:

$$C_4H_3(COHO)O + C_6H_5NH_2 = C_{10}H_7NH_2 + H_2O + CO_2 \quad (5)$$

To enhance the mechanical stability of chromatographic plates, binding agents may be used. In earlier practices, for example**,** gypsum (up to 13% by mass) was widely employed in plates containing G-grade silica gel**.** In modern commercially available thin-layer chromatography (TLC) plates, organic binders such as methacrylate's are commonly utilized. Literature sources also describe the application of starch and carboxymethylcellulose as alternative binding materials.

In the TLC experiments we conducted, the eluent functioned as the mobile phase**.** During eluent selection, we based our choice on the solubility characteristics of the synthesized product in various solvents. A 1:1 mixture of benzene and acetone was prepared as the eluent to optimize the separation and visualization of spots formed on the TLC plate surface. This eluent composition proved effective in facilitating compound migration during analysis.

We plan to continue using this eluent composition in future TLC analyses, particularly because cytosine exhibits greater solubility in benzene than in acetone**,** which significantly influences the chromatographic behavior of certain derivatives. The synthesis of naphthylamine derivatives was performed using TLC as a method to monitor the reaction progress and analyze product purity, particularly in reactions involving acrylic acid.

The synthesized product was analyzed via TLC using pure benzene and acetone as the eluent system. A spot of naphthylamide of acrylic acid was applied at the first chromatographic point, while a spot of hydrazine hydrate-modified naphthylamide of acrylic acid was applied at the second point.

Figure 1.

Figure 1. TLC analysis of naphthylamide derivatives of acrylic acid.
Spot 1: Acrylic acid naphthylamide
Spot 2: Hydrazine hydrate-modified acrylic acid naphthylamide
Eluent system: Benzene : Acetone = 1 : 1
Observed R_f value: 3.7

Research Results: Based on the conducted experimental work, the obtained results demonstrate promising potential for application in the chemical industry, particularly in the synthesis of dyes and organic intermediates. It is well known that the reactivity and biological properties of chemical compounds are significantly influenced by the nature and position of substituent groups located in close proximity to active molecular centers. According to the experimental procedure, the synthesis began with the distillation of acrylic acid anhydride using a vacuum water jet pump to obtain naphthylamide of acrylic acid via a synthetic route. The resulting compound was then analyzed using thin-layer chromatography (TLC). Subsequently, this naphthylamide was treated with hydrazine hydrate, producing a novel compound—hydrazine-hydrate-modified naphthylamide of acrylic acid—which was again verified by TLC. These final products were further characterized using spectrometric techniques, aiming to evaluate their significance and potential applications in chemical research and industry.

Conclusion. This study provided a comprehensive overview of naphthylamine and its derivatives, focusing on the synthesis pathways and practical significance of these compounds. The main objective was to explore the possibility of obtaining new naphthylamine derivatives through chemical synthesis. In chemistry, synthesis plays a critical role in transforming relatively simple compounds into more complex substances. Traditionally, synthetic compounds are obtained by combining or rearranging the molecular structures of simpler precursors, in contrast to naturally occurring substances. Examples include synthetic rubber, synthetic fibers, synthetic detergents, and synthetic fuels.

Notably, chemical synthesis is not limited to mimicking natural compounds—it also enables the creation of entirely novel molecules not found in nature. As a foundational discipline within industrial chemistry, synthetic methodologies underpin various sectors of chemical technology. Specialists in this field have long focused on the targeted synthesis of specific chemical products. As a subfield, basic organic synthesis includes the large-scale production of alcohols, acids, ethers, aldehydes, and other essential organic compounds. In the domain of petrochemical synthesis, researchers develop technologies for converting petroleum raw materials into a diverse array of chemical products. Alongside chemical synthesis, the biosynthesis of complex organic molecules is gaining attention through the use of enzymatic and microbial methods, which rely on natural catalysts (enzymes) and microorganisms. For instance, the production of glucose from plant biomass has been successfully achieved via enzymatic synthesis, whereas its chemical synthesis remains too complex. Additionally, microbial conversion of paraffins into protein-rich biomass has proven to be economically viable. These innovations highlight the emergence of microbiological industry, a new field at the intersection of chemistry and biology.

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НАФТИЛАМИН И ЕГО ПРОИЗВОДНЫЕ

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Аннотация. В статье рассматривается изучение органического вещества нафтиламина, основного производного нафталина, и его производных, их свойств, а также их синтеза в различных направлениях.

Нафтиламин и его производные используются в различных целях в химической промышленности. Нафтиламин относится к группе первичных аминов и является одним из производных нафталина.

В статье представлен химический метод синтеза нафтиламина. Химический синтез — процесс создания или образования сложных молекул, а также получения химических соединений физическими и химическими методами. В органическом синтезе конечным результатом химической реакции может быть более простое вещество, чем исходное соединение. Развитие органического синтеза является прорывом в сельском хозяйстве, медицине, парфюмерии, пищевой промышленности и т. д. стр. Возможность получения различных активных веществ, используемых в таких областях, как Усовершенствования методов синтеза сделали возможным получение многих востребованных химических веществ в промышленных масштабах. В органической химии это может быть синтез аммиака, соды, серной и азотной кислот, а также других соединений. В статье рассматриваются химические и физические свойства нафтиламина — аминопроизводного нафталина, а также его применение в различных отраслях промышленности. Приведена информация о двух изомерах нафтиламина: 1-нафтиламин (α-нафтиламин) и 2-нафтиламин (β-нафтиламин). В статье рассматриваются области применения нафтиламинов, в частности их роль в синтезе красителей, фармацевтических препаратов и других органических соединений. Особое внимание уделено канцерогенным свойствам 2-нафтиламина, его опасности для здоровья человека, а также мерам безопасности, которые необходимо соблюдать при работе с этими соединениями. Цель статьи — расширить знания о свойствах и применении нафтиламина, а также понять важность соблюдения мер предосторожности при работе с ним.

Ключевые слова: анилин, синтез, соединение, производное, процесс, нафтиламин, хроматография, амин.

НАФТИЛАМИН ЖӘНЕ ОНЫҢ ТУЫНДЫЛАРЫ

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Аңдатпа. Бұл мақалада нафталинның басты туындысы болып табылатын органикалық зат нафтиламин және оның туындыларын, қасиеттерін зерттеу және әр түрлі бағытта синтездеп алу.

Нафтиламин және оның туындылары химиялық саланың әртүрлі мақсатына қолданылады. Нафтиламин біріншілік амин тобына жатады және нафталин туындыларының бірі болып таблады.

Мақалада нафтиламинге химиялық синтез әдісі жүргізіледі. Химиялық синтез - бұл күрделі молекулаларды құру немесе жасау процесі, сондай-ақ физикалық және химиялық әдістермен химиялық қосылыстарды алу. Органикалық синтезде химиялық реакцияның соңғы нәтижесі оның бастапқы қосылысына қарағанда қарапайым зат болуы мүмкін. Органикалық синтезді дамыту - бұл ауыл шаруашылығы, медицина, парфюмерия, тамақ өнеркәсібі және т. б. сияқты бағыттарда қолданылатын түрлі белсенді заттарды алу мүмкіндігі. Синтетикалық әдістерді жетілдіру өнеркәсіптік ауқымда көптеген қажетті химиялық заттарды алуға мүмкіндік берді. Органикалық химияда бұл аммиак, сода, күкірт және азот қышқылы, сондай-ақ басқа да қосылыстар синтезі болуы мүмкін. Бұл мақалада нафтиламин, яғни нафталиннің амин туындыларының химиялық және физикалық қасиеттері, сондай-ақ олардың әртүрлі салаларда қолданылуы қарастырылады. Нафтиламиннің екі изомері: 1-нафтиламин (α-нафтиламин) және 2-нафтиламин (β-нафтиламин) туралы ақпарат беріледі. Мақалада нафтиламиндердің қолданылу аясы, атап айтқанда, бояғыштар, фармацевтикалық препараттар және басқа да органикалық қосылыстарды синтездеудегі рөлі талқыланады. Ерекше назар 2-нафтиламиннің канцерогендік қасиеттеріне аударылады, оның адам денсаулығына төндіретін қауіптері мен осы қосылыстармен жұмыс істеу кезінде сақталуы тиіс қауіпсіздік шаралары көрсетіледі. Мақала нафтиламиннің қасиеттері мен қолданылуы туралы білімді кеңейтуге және олармен жұмыс істегенде қауіпсіздік ережелерін сақтаудың маңыздылығын түсінуге арналған.

Түйін сөздер: анилин, синтез, қосылыс, туынды, процесс, нафтиламин, храмотография, амин.