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Review Article

Naphthalene Derivatives: Emerging Trends In Chemistry, Synthesis And Medicinal Applications

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Abstract

Naphthalene, a basic bicyclic aromatic hydrocarbon, serves as a valuable framework in medicinal chemistry because of its diverse range of biological activities. Naturally occurring and synthetic naphthalene derivatives exhibit potent pharmacological effects, including anti-HIV, anticancer, antitubercular, antimicrobial, anti-inflammatory, antihypertensive, antidiabetic, antiviral, and neuroprotective properties. Compounds like rifampicin, naproxen, and Bedaquiline underscore its therapeutic relevance. Various synthetic methods, including the Haworth synthesis and petroleum cracking, facilitate naphthalene production. Naphthalene's unique physicochemical features such as high photostability, π-electron conjugation, and fluorescence enable its use in both drug design and material science. Its reactivity in electrophilic substitution reactions (nitration, sulphonation, halogenation) allows for diverse structural modifications, enhancing bioactivity. Recent research highlights naphthalene-based hybrids showing promise in combating drug resistance, inflammation, cancer, and neurodegeneration. Additionally, FDA-approved drugs like propranolol and duloxetine further establish its clinical utility. Overall, naphthalene remains a crucial molecular framework in developing innovative therapeutic agents and biomedical applications.

Keywords: Naphthalene, Substituted benzoic acids, α and β naphthol, Anti-microbial activities, Anti-inflammatory, Anti-cancer activity, Esterification

Introduction

Naphthalene has gained considerable attention as a flexible framework in medicinal chemistry, serving as an important structural unit in drug discovery because of the diverse biological activities derived from its modifications. A number of naturally occurring molecules containing the naphthalene core exhibit significant pharmacological effects. For instance, Patentiflorin shows anti-HIV potential, justicidin demonstrates anticancer activity, Rifampicin is widely used in tuberculosis therapy, and bis-ANS 82 functions as an inhibitor of tubulin polymerization. Notably, in 2018, Kittakoop and collaborators reported the isolation of several naphthalene derivatives from

Ventilago denticulata, which revealed both antibacterial and cytotoxic properties along with inhibitory effects on aromatase and phosphodiesterase. Moreover, the naphthalene structure is present in several widely available medications, such as Bedaquiline, naproxen, Nafimidone, and Nafcillin, highlighting its relevance and potential in therapeutic applications [1].

Naphthalene, a solid polycyclic aromatic hydrocarbon, has traditionally been produced through simple distillation from coal tar. More advanced methods, such as the Jaureg process, allow for the synthesis of phenyl-substituted naphthalene, expanding its range of applications. Over the past few decades, both academic and industrial research has increasingly focused on organic molecules, particularly those with conjugated ring systems like naphthalene. In addition to its industrial uses, naphthalene has been linked to several bioactive phytoconstituents. Notably, compounds like bis-ANS 82, which acts as an alkylating agent, demonstrate significant inhibitory effects on tubulin polymerization. Furthermore, certain naphthalene derivatives have been developed into anticancer drugs, including podophyllotoxins such as etoposide and Teniposide. These compounds highlight the cytotoxic properties of naphthalene and its derivatives, which are being explored for their potential in medicinal applications [2].

Many plants' essential oils naturally include naphthalene, a white crystalline substance with a polycyclic aromatic hydrocarbon and distinctive mothball structure. Derivatives of naphthalene are widely used as insecticides, wetting agents, and surfactants, among other pharmaceutical applications. These derivatives have special chemical and photophysical characteristics. They are the most researched class of organic compounds because of these features. Naphthalene dyes feature a large π-electron conjugation and a stiff plane. As a result, they have outstanding photostability and a high quantum yield. Because they are hydrophobic, fluorescent probes based on naphthalene have exceptional sensing and selectivity capabilities toward anions and cations. They can also be incorporated into target biomolecules. The addition of a naphthalene moiety improved the conjugated probe system's photo-stability. Naphthalene derivatives are therefore regarded as a great option among other conjugated frameworks for the development of organic electrical goods. These compounds' potent fluorescence, electroactivity, and photostability make them valuable for a range of applications [3]

Physical Properties of Naphthalene:

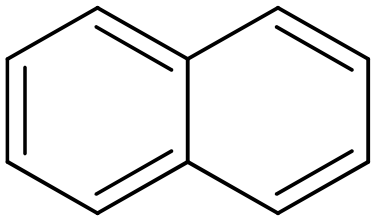

Figure 01: Naphthalene

Table 01: Physical Properties of Naphthalene

Property	Value
Chemical Formula	$C_{10}H_8$
Molar Mass	128.17 g/mol
Appearance	White crystalline solid
Odour	Strong, mothball-like odour
Melting Point	80.2 °C (176.4 °F)
Boiling Point	218 °C (424.4 °F)
Density	1.14 g/cm³ at 20 °C
Solubility in Water	Very low (~0.03 g/L at 25 °C)
Solubility in Solvents	Soluble in benzene, ether, chloroform, alcohol

Resonance:

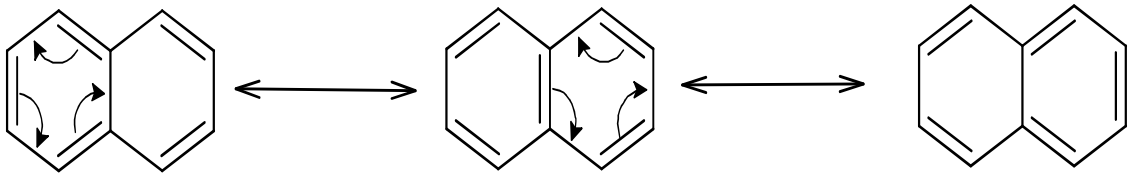

Figure 02: Resonance

Different Methods involved in preparation of naphthalene

Synthesis of Naphthalene from Haworth Synthesis:[4]

In this synthetic approach, benzene undergoes a Friedel–Crafts reaction with succinic anhydride to form the corresponding acid, which is then reduced under Clemmensen conditions. The intermediate subsequently cyclizes to α-tetralone, and through further reduction followed by dehydrogenation, naphthalene is obtained.

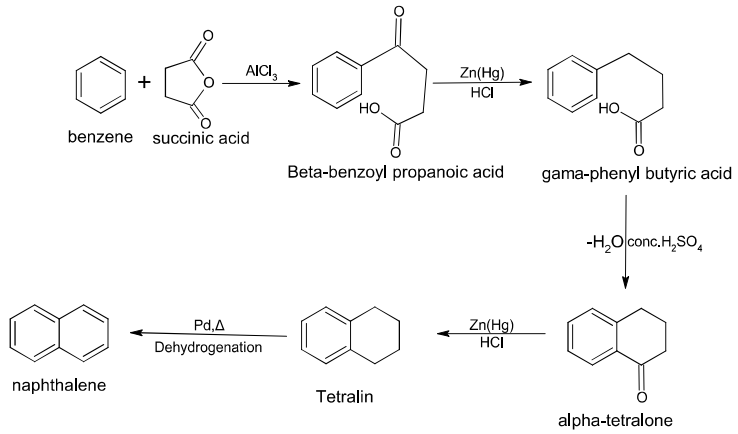

Figure 03: Synthesis of Naphthalene from Haworth Synthesis

Preparation of Naphthalene from 4-Phenylbut-1-ene

Naphthalene can be synthesized from 4-phenyl-1-butene by passing the compound over heated calcium oxide at high temperatures. [5]

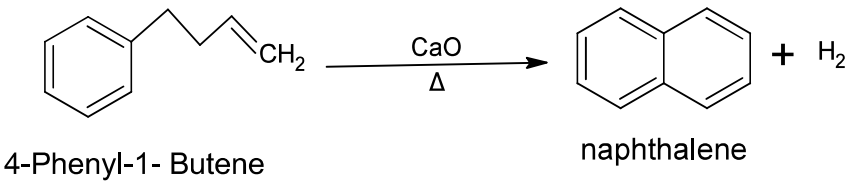

Figure 04: Preparation of Naphthalene from 4-Phenylbut-1-ene

Preparation of Naphthalene from 4-Phenyl-3-butanoic Acid:

When 4-phenyl-3-butanoic acid is heated with concentrated sulfuric acid, it produces 1-naphthol, which upon distillation with zinc dust gives naphthalene. [5]

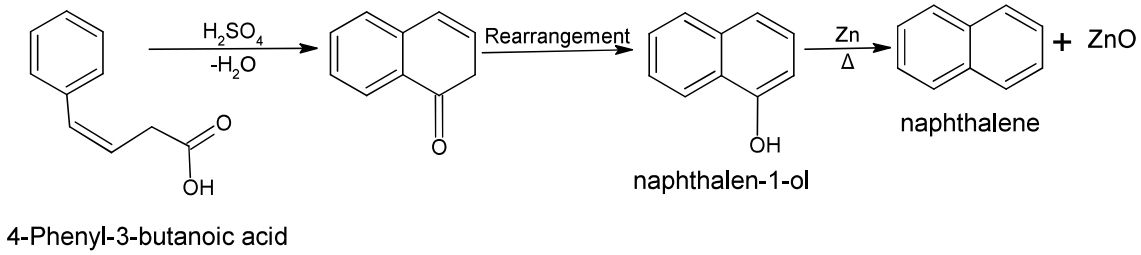

Figure 05: Preparation of Naphthalene from 4-Phenyl-3-butanoic Acid

Preparation of Naphthalene from 3-benzoylpropanoic Acid:

Heating 3-benzoylpropanoic acid with sulfuric acid yields naphthol, which upon distillation with zinc dust is converted into naphthalene. [6]

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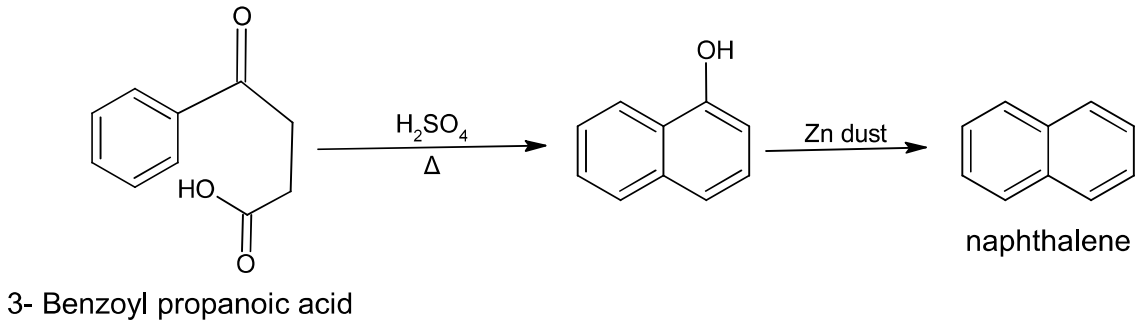


Figure 06: Preparation of Naphthalene from 3-benzoylpropanoic Acid

Synthesis of Naphthalene from Petroleum:

High-temperature catalytic cracking of a petroleum fraction to produce naphthalene and methyl-naphthalene. [7]

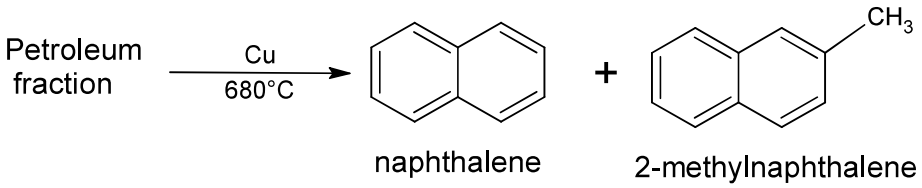


Figure 07: Synthesis of Naphthalene from Petroleum

Chemical reactions:

A. Oxidation reaction of naphthalene:

1. In an acidic media containing potassium permanganate, naphthalene oxidizes to produce phthalic acid.

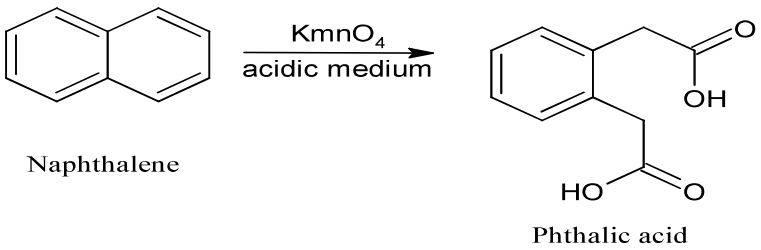


Figure 08: Oxidation reaction of naphthalene (acidic medium)

2. In a basic media containing potassium permanganate, naphthalene oxidizes to produce phthalonic acid.

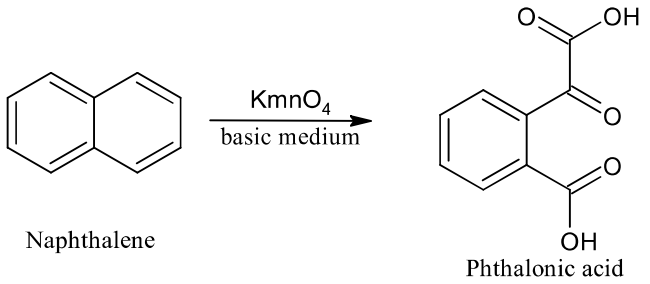


Figure 09: Oxidation reaction of naphthalene (basic medium)

3. Naphthalene undergoes oxidation in presence of chromic acid to produces 1,4-naphtoquilone.

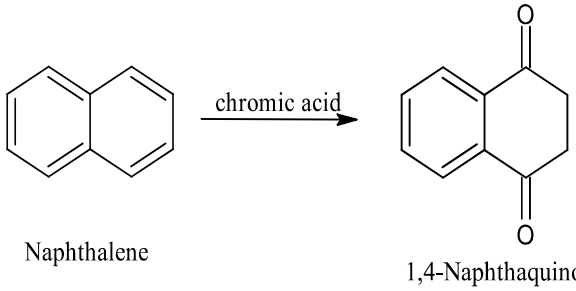


Figure 10: Oxidation reaction of naphthalene (chromic acid)

4. Naphthalene undergoes oxidation in presence of zinc and ozone to form Phthalaldehyde

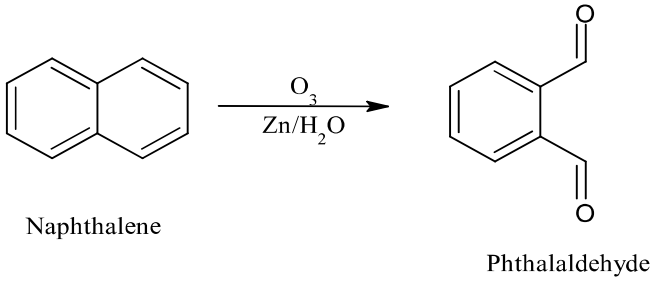


Figure 11: Oxidation reaction of naphthalene (Zn/H2O)

5. Naphthalene undergoes oxidation in presence of sulphuric acid and mercuric sulphate to form phthalic anhydride. [8]

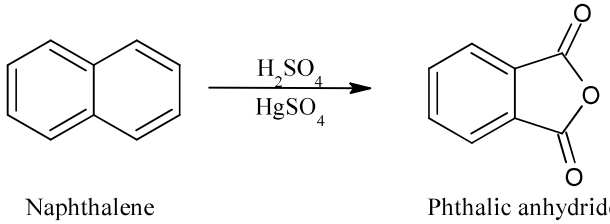


Figure 12: Oxidation reaction of naphthalene (H2SO4)

B. Reduction reaction of naphthalene:

1. Naphthalene undergoes reduction in presence of hydrogen and nickel to from Tetralin which further undergo reduction to form Decalin.

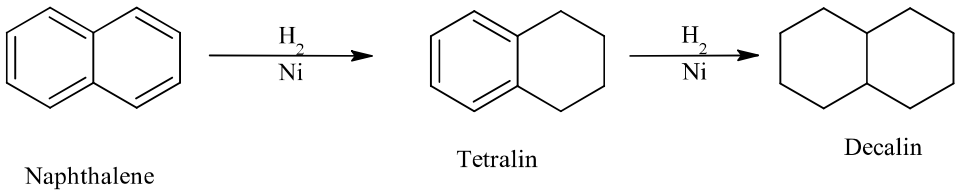


Figure 13: **Reduction reaction of naphthalene (hydrogen and nickel)**

2. Naphthalene undergoes reduction in presence of sodium metal and isopentanol to form Tetralin.

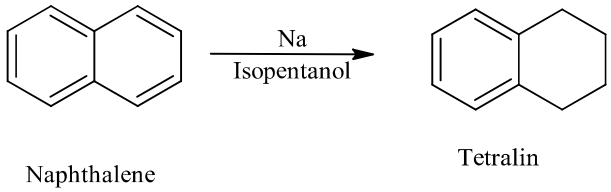


Figure 14: **Reduction reaction of naphthalene (sodium metal and isopentanol)**

3. Naphthalene undergoes reduction in presence of sodium metal and ethanol to form 1,4- Dialin.

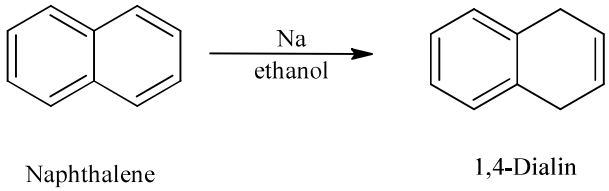


Figure 15: **Reduction reaction of naphthalene (sodium metal and ethanol)**

4. Naphthalene undergoes reduction in presence of hydrogen and platinum metal to form Decalin.

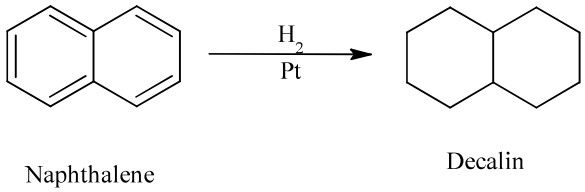


Figure 16: **Reduction reaction of naphthalene (hydrogen and platinum metal)**

C. Addition reaction:

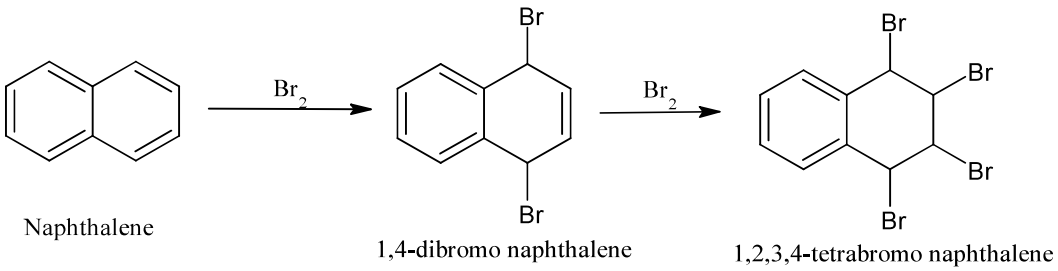


Figure 17: **Addition reaction of naphthalene**

The addition of chlorine or bromine to naphthalene produces naphthalene dichloride or naphthalene dibromide. With further halogen addition, naphthalene tetrachloride or naphthalene tetrabromide is formed.

D. Nitration reaction:

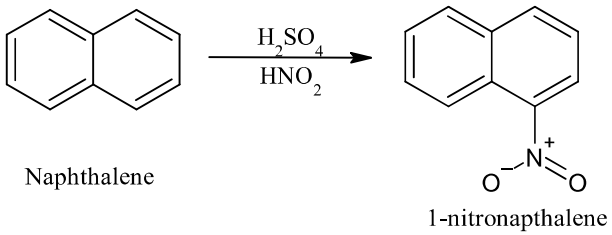


Figure 18: **Nitration reaction**

Under electrophilic aromatic substitution conditions, reaction of naphthalene with a mixture of nitric acid and sulfuric acid at low temperature predominantly yields α-nitronaphthalene.

E. Halogenation reaction:

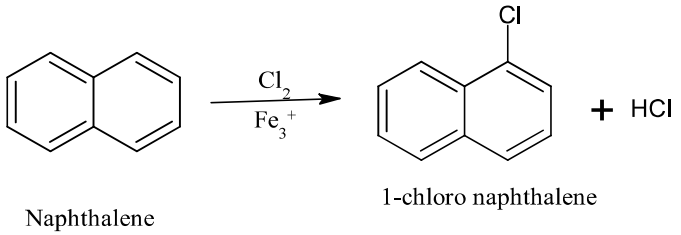


Figure 19: **Halogenation reaction**

When a Lewis acid catalyst, such as iron (Fe), is present, naphthalene and chlorine react to produce α-chloronaphthalene as the main product and hydrogen chloride (HCl) as a byproduct.

F. Sulphonation reaction:

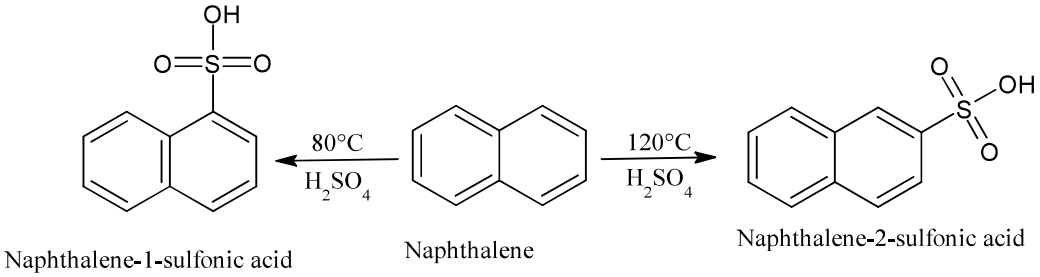


Figure 20: **Sulphonation reaction**

Another electrophilic substitution process that involves adding a sulfonic acid group (SO_3H) to the aromatic ring is sulphonation. Kinetic control promotes the synthesis of naphthalene-1-sulfonic acid at lower temperatures (e.g., 80°C). Higher temperatures (such as 120°C) result in thermodynamic control, which makes naphthalene-2-sulfonic acid, which is more stable, the main product.

G. Friedel-crafts alkylation:

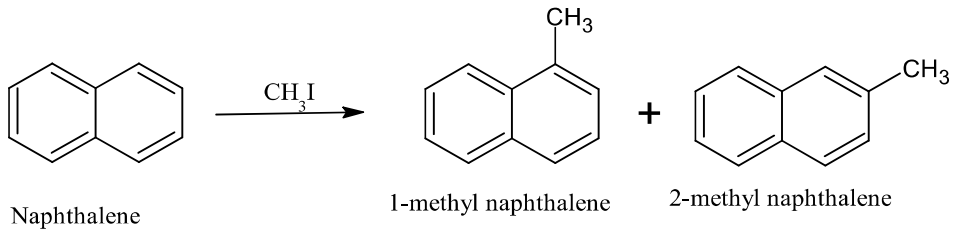


Figure 21: **Friedel-crafts alkylation**

In a Friedel–Crafts alkylation, an alkyl substituent is introduced onto an aromatic system. When naphthalene undergoes this reaction at low temperature with an alkylating reagent (for example, methyl chloride or a similar methyl donor) in the presence of a Lewis acid catalyst like $AlCl_3$, two main products are obtained: the major product is 1-methylnaphthalene, while the minor one is 2-methylnaphthalene.

H. Friedel-crafts acylation:

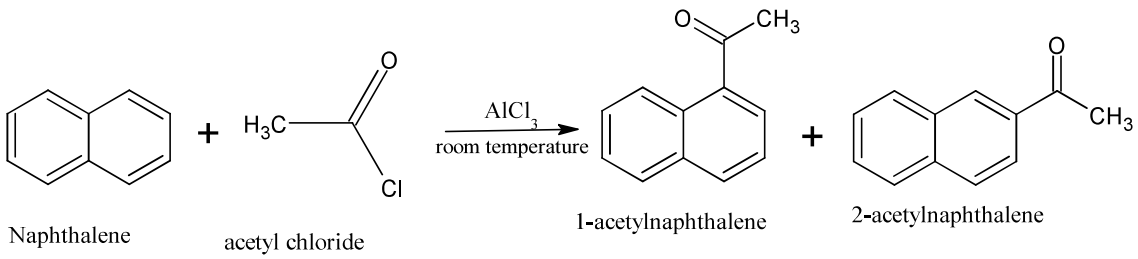


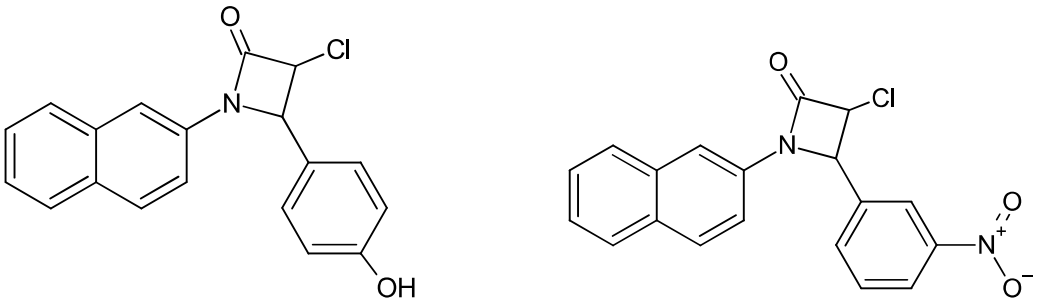
Figure 22: **Friedel-crafts acylation**

When naphthalene undergoes electrophilic substitution reaction in presence Of acetyl chloride, Aluminium chloride as catalyst at room temperature to Produce 1-Acetylnaphthalene and 2-acetylnaphthalene. [9]

Biological activities of naphthalene & derivatives:

1. Anti-microbial activity:

- Mustafa, Khalil *et al,* "The effect of aryl and heteroaryl conjugation on the biological activities of naphthalene: A review." As the use of antibacterial medications rises, the prevalence of antibiotic-resistant bacteria grow. To combat these bacteria that are resistant to antibiotics, this situation requires research and effective creation of new antibacterial agents. [10]
- Ersan, Yuksel *et al,* "One-pot synthesis of novel benzimidazoles with a naphthalene moiety as antimicrobial agents and molecular docking studies." Numerous studies have demonstrated that a naphthalene ring possesses antibacterial properties against both bacterial and fungal strains. [11]
- Bhawna Chopra *et al.* "Synthesis and antimicrobial activity of naphthylamine analogues having azetidinone and thiazolidinone moiety." artificially produced naphthylamine analogues with an azetidinone moiety for antibacterial properties. Compounds (1) and (2) demonstrated wide-ranging activity against Pseudomonas aeruginosa, Escherichia coli, Staphylococcus aureus, and Bacillus subtilis. [12]



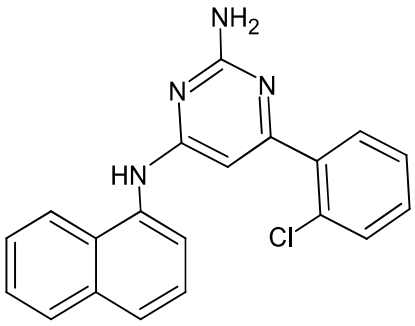
(1) **(2)**

Figure 22. Chemical structures of naphthylamine derivatives (1) and (2) containing azetidinone and thiazolidinone moieties with reported antimicrobial activity

2. Anti-inflammatory effect:

- Medzhitov *et al,* "Origin and physiological roles of inflammation." Currently, the naphthalene derivatives naproxen and nabumetone are utilized to treat inflammatory diseases. [13]

- V. Muralidharan *et al.* "Synthesis and characterization of some novel naphthalene-pyrimidine derivatives as anti-inflammatory agents have created new compounds by combining naphthalene and pyrimidine, which have shown impressive anti-inflammatory effects. These compounds were designed to target specific pathways involved in inflammation, and one particular compound demonstrated exceptional potency.
- The fusion of naphthalene and pyrimidine is significant since both frameworks are linked to diverse biological activities such as anti-inflammatory, anticancer, and antimicrobial effects. [14]

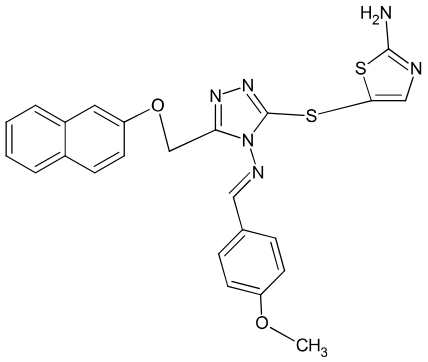


(3)

Figure 23. Chemical structure of a novel naphthalene–pyrimidine derivative (3) designed for anti-inflammatory activity.

- Elrayess *et al.* "Synthesis, 3D-QSAR, and Molecular Modelling Studies of Triazole Bearing Compounds as a Promising Scaffold for Cyclooxygenase-2 Inhibition .A study on the design, 3D-QSAR, and molecular modelling of triazole-based compounds introduced aryl and heteroaryl frameworks to generate a new series of triazole Schiff base derivatives was developed and tested for

their ability to inhibit COX-2.Results from the COX-2 inhibition assay revealed that the triazole–thiazole hybrid containing a para-methoxy group on the phenyl ring (compound 4) demonstrated the strongest *in vitro* selectivity (IC_{50} = 0.04 μM) and significant *in situ* anti-inflammatory activity (IC_{50} = 0.88 μM), showing comparable potency to the marketed COX-2 inhibitor Celecoxib (IC_{50} = 0.05 μM). [15]

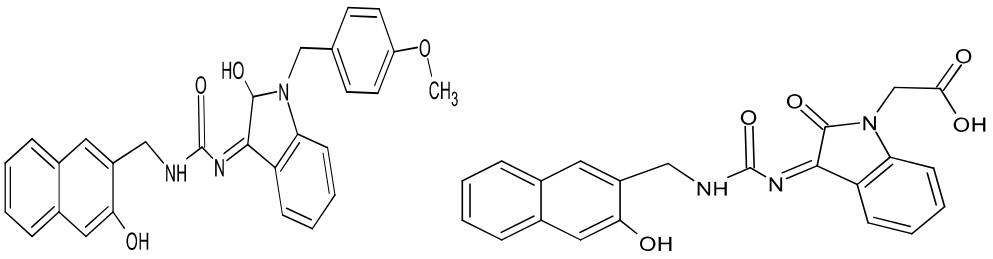


(4)

Figure 24. Chemical structure of triazole–thiazole hybrid compound (4) exhibiting potent COX-2 inhibitory and anti-inflammatory activity

3. Antihypertensive activity:

- Bekhradnia and Ebrahimzadeh *et al,* "Theoretical study on some non-selective beta-adrenergic antagonists and correlation to their biologically active configurations." Two examples of non- selective β-adrenergic blockers commonly prescribed for hypertension are propranolol, which is structurally derived from naphthalene, and nadolol, which originates from tetrahydro-naphthalene. [16]
- Manikandan *et al.* "Therapeutic investigations of novel indoxyl-based indolines: A drug target validation and Structure-Activity Relationship of angiotensin-converting enzyme inhibitors with cardiovascular regulation and thrombolytic potential." a range of naphthalene derivatives was evaluated for inhibitory effects on angiotensin-converting enzyme (ACE). Among these, compounds 5 and 6, which incorporated a naphthalene-linked oxo-indoline framework, showed significant ACE inhibition. [17]

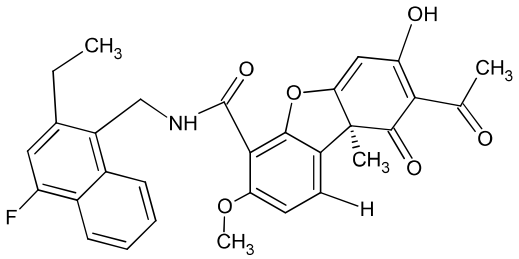


(5) **(6)**

Figure 25. Chemical structures of naphthalene-based derivatives (5) and (6) exhibiting significant angiotensin-converting enzyme (ACE) inhibitory and antihypertensive activity.

4. Anti-diabetic activity:

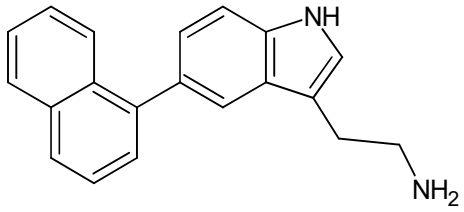
- Okur, Karantas *et al,* "Diabetes mellitus: A review on pathophysiology, current status of oral medications and future perspectives." The chronic metabolic disease known as diabetes mellitus (DM) is typified by hyperglycaemia, or abnormally elevated blood glucose levels. Diabetes damages most of the organs, and nerves, which can lead to long-term issues. [18]
- Furukawa *et al.* "Synthesis and biological evaluation of novel (−)-cercosporamide derivatives as potent selective PPARγ modulators." Synthesized compound (7) which demonstrated strong agonistic action and reduced blood sugar levels. In particular, it exhibited PPAṘ agonist action, and its potassium salt was nearly as effective as rosiglitazone. [19]



(7)

Figure 26. Chemical structure of (−)-cerosporamide derivative (compound 7) exhibiting potent PPARγ agonistic and antidiabetic activity.

- Patch *et al.* "Identification of diaryl ether-based ligands for estrogen-related receptor α as potential antidiabetic agents." discovered that compound (8) possesses anti-diabetic property. [20]
-



(8)

Figure 27 Structure of diaryl ether-based ligand (compound 8) reported to possess antidiabetic activity through estrogen-related receptor α modulation.

5. Anti-cancer activity:

- L. Luo *et al.* "Synthesis and anticancer activity evaluation of naphthalene-substituted triazole spirodienones." produced a number of new triazole spirodienones substituted with naphthalene and assessed their antitumor properties. Through the induction of cell cycle arrest and death, compound (9) demonstrated the strongest anti-cancer effect. Additionally, compound (9) dramatically reduced tumour growth in a 4T1murine model of metastatic breast cancer. [21]
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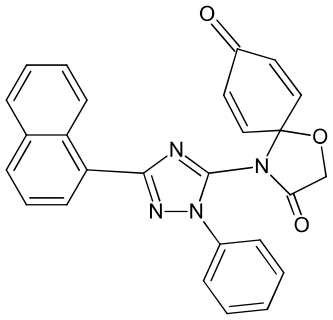
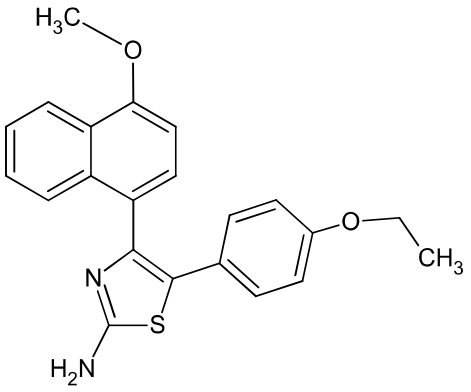


(9)

Figure 28. Chemical structure of naphthalene-based compound (9) exhibiting significant anticancer activity and tumor growth inhibition in a 4T1 murine metastatic breast cancer model.

- G. Wang *et al.* "Design, synthesis and biological evaluation of novel thiazole-naphthalene derivatives as potential anticancer agents and tubulin polymerization inhibitors." produced a new class of thiazole-naphthalene compounds to inhibit tubulin polymerization and assessed their anti-proliferative properties. When compared with the standard drug, compound 10 displayed superior potency and strongly inhibited tubulin polymerization, achieving an IC_{50} in the micromolar range. [22]

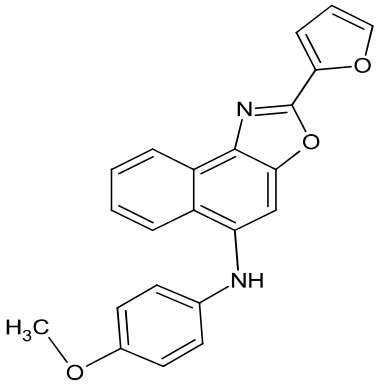


(10)

Figure 29. Chemical structure of thiazole–naphthalene derivative (compound 10) showing potent antiproliferative activity through tubulin polymerization inhibition.

6. Antiviral activity:

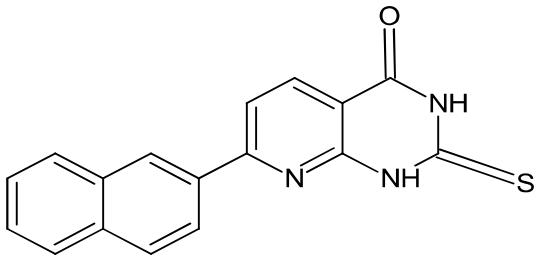
- Tseng *et al,* "Discovery of naphtho [1, 2-d] oxazole derivatives as potential anti-HCV agents through inducing heme-oxygenase-1 expression." naphtho [1,2-d] oxazole compounds and assessed their anti-HCV efficacy by inducing the production of heme-oxygenase-1. Compound (11) was the most potent of the produced compounds, with 21 times the anti-HCV activity of ribavirin. [23]



(11)

Figure 30. Chemical structure of naphthalene–heterocycle hybrid (compound 11) evaluated for antiviral activity.

- Mohamed A. Elsayed *et al,* "Synthesis, Molecular Docking, DFT and Pharmacophore Studies of New Naphthalene-Heterocycle Hybrids of Prospective Antiviral Activity." the chemical structure of the synthesized compounds **(12)** shows anti-viral activities. [24]

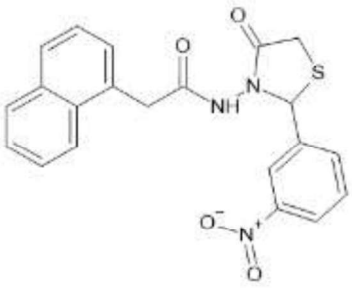


(12)

Figure 31. Chemical structure of naphthalene-based compound (12) demonstrating significant antiviral activity.

7. Anti-neurodegenerative activity:

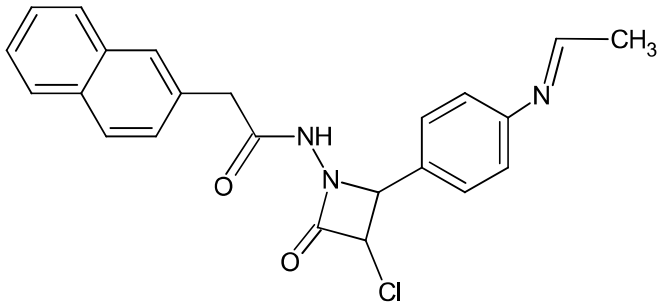
- Ayeni, Gong *et al,* "Medicinal plants for anti-neurodegenerative diseases in West Africa." Neurodegenerative disorders are neuronal diseases that progressively degenerate the structure and function of either the peripheral or central nervous system, affecting the components of the brain. It is a leading cause of death and affects a large number of people around the world. [25]



(13)

Figure 32. Chemical structure of naphthalene-derived compound (13) investigated for anti-neurodegenerative potential.

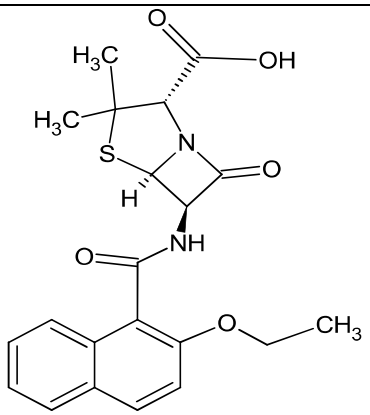
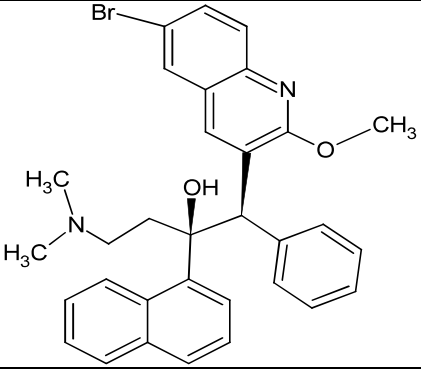
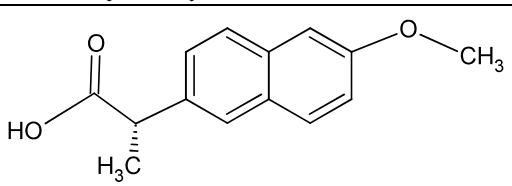
- G Subramanian *et al,* **"**Synthesis and biological evaluation of the selected naphthalene substituted azetidinone derivatives targeting Parkinson's disease." The synthesis of compound (14) produced a satisfactory synthetic yield. For the produced compounds, IR and 1H-NMR were performed, and structures were determined. The produced chemicals were tested for their ability to prevent Parkinson's disease. Compound (14) underwent an in vitro experiment for scavenging free radicals. Compounds (14) have demonstrated a favorable outcome in that regard. [26]

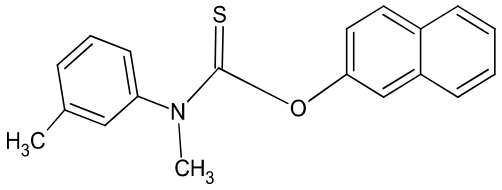
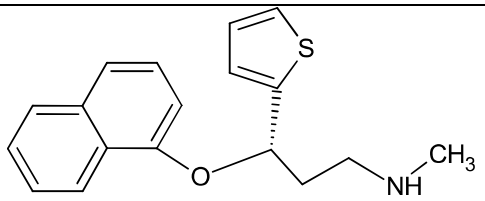
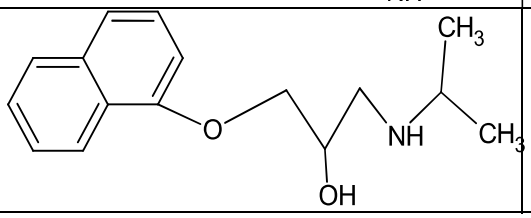


(14)

Figure 33. Chemical structure of naphthalene-substituted azetidinone derivative (compound 14) evaluated for anti-Parkinson's and free radical scavenging activity.

Table 02: Some Novel Naphthalene Derivatives and their Medicinal Uses:

Serial Number	Compound Name	Compound Structure	Medicinal Uses
1	NAFCILLIN		It is used as Anti-biotic agent.
2	BEDAQUILINE		It is used as Anti-tubercular agent.
3	NAPROXEN		It is used as Anti-inflammatory agent.

4	TOLNAFTATE		It is used as Anti-fungal agent.
5	DULOXETINE		It is used as Anti-depression and anxiety.
6	PROPANOLOL		It is used as Beta blocker. [27]

Conclusion:

Multiple naphthalene derivatives have been synthesized through diverse synthetic approaches, and many of these compounds exhibit noteworthy pharmacological properties. Naphthalene, as a key organic scaffold, demonstrates a wide range of biological activities, particularly against cancer, diabetes, hypertension, inflammation, malaria, as well as microbial, fungal, and viral infections. Owing to this broad therapeutic potential, naphthalene has attracted significant interest from researchers seeking novel biologically active molecules. Overall, this review highlights that naphthalene possesses a versatile spectrum of biological effects and holds considerable promise for further exploration. Additionally, the described synthetic strategies for naphthalene-based compounds provide valuable guidance for chemists in designing and developing innovative drug-like agents for the management of various diseases and disorders.

Conflict of Interest

The Authors declares no conflict of interest.

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