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"Synthesis and Characterization of Hydrazine Derivatives."

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Abstract: Hydrazine-based derivatives are an important class of compounds in synthetic and medicinal chemistry, not only because of their diverse chemical reactivity, but also because of their broad spectrum of biological and industrial uses. These compounds possess an interesting pharmacological profile due to the presence of the –NH–NH_2 group that permits a variety of synthetic processes such as condensations, cyclizations and substitutions. The considerable structural versatility of hydrazine-based frameworks makes them popular in pharmaceuticals, agrochemicals, dyes, corrosion inhibitors and energetic materials. This paper aims to review the different types of synthetic methods used for the synthesis of hydrazine derivatives including classical methods and modern methods (such as solvent-free reaction, microwave-assisted synthesis and green chemistry routes). Additionally, sophisticated characterization techniques such as spectroscopic methods (NMR, IR, UV-Vis) and chromatographic and crystallographic measurements are covered in detail with their novelty in guaranteeing structural identification and purity_relying. Highlights are presented on new progress in structure-activity correlations (SAR) and bioactivity, (in particular: on antimicrobial, anticancer, anti-inflammatory actions). The review also gives insight on the rising applications and the future potential of hydrazine chemistry in drug discovery and material science. This review is intended as a reference source for scientists working in the field of design and function of hydrazine-based derivatives that critically analyse and compile the recent literature.

Keywords: discovery, guaranteeing, compile, chromatographic

Introduction

Hydrazine (N2H4) and its derivatives are an important group of nitrogen-containing compounds, which played an important role in the synthetic organic chemistry, medicinal chemistry and materials science. Hydrazine history's Hydrazine was first synthesised in 1887 by Theodor Curtius. Deemed little more than a curiousity in the realm of inorganic chemistry, hydrazine rapidly became indispensable owing to its remarkable nucleophilicity and reducing characteristics. Hydrazine can be a versatile building block, as it can be easily transformed into a variety of structurally different compounds. There is a vast variety of hydrazine-based molecules, such as hydrazones, azines, acylhydrazides, and heterocyclic derivatives which have been synthesized over the past decades with interesting biological and physicochemical profiles.

On a structural level, hydrazine is a little more than two nitrogen atoms linked together by a single bond and carrying four hydrogen atoms on it terminals. Such a simple structure belies the molecule's rich reactivity and application. The derivative hydrazine compounds, when functionalized via substitution or condensation reactions, can introduce characteristics like improved thermal stability, e-donating ability and H bonding capacity. These attributes render the hydrazine-based compounds attractive as intermediates of pharmaceutic, agrochemical and special polymers. Even more, the hydrazine group is bifunctional with two reactive sites and it is highly compatible for conjugation with numerous kind of electrophiles, which makes it suitable for multi-step synthetic approaches.

The hydrazine derivatives have attracted a growing interest over the last two decades because of their proved potentiality as the pharmacophores in drug discovery. Agents such as isoniazid (antitubercular), phenelzine (antidepressant) and cefazolin (antibiotic) contain hydrazine-based sub-structures and represent well accepted examples of therapeutic utility. More recently, derivatives of hydrazines were tested for antimicrobacterial, anticancer, antimalarial and anti-inflammatory activity. These discoveries have spurred medicinal chemists to explore the SAR around the hydrazine core, with an aim to enhance the potency, selectivity, and pharmacokinetics.

The developments of hydrazine chemistry have been described in various review papers and monographs. For example, the previous studies have been mainly limited to reaction mechanisms, nucleophilicity, and synthetic reactions with hydrazines. There are voluminous reports on the topics of toxicology and safety of hydrazine handling as well. In the 2010s, the spotlight on green chemistry became stronger with studies focusing on catalyst under green conditions, and solvent-free synthesis. But these previous reviews are relatively narrow in scope, or relatively outdated add to the interest boom since 2020. Recent advances have not been critically discussed, particularly regarding the transition of hydrazine chemistry into nanotechnology, green chemistry and drug delivery applicability.

Thus, this review aims to offer a current and comprehensive summary of synthetic strategies, characterization techniques, and various applications of hydrazine derivatives. The overall aim is to narrow the gap that separates traditional synthetic methods from modern tendencies in hydrazine chemistry. The review aims to cover up-to-date synthetic methodologies, such metal-catalyzed reactions, multi-component reactions and green procedures, as well as a critical review of analytical methods, such NMR, FT-IR, MS and single-crystal X-ray diffraction. Moreover, the review also emphasizes on the medicinal, agricultural and industrial significance of these compounds, description of market relevance and the latest patents.

To achieve that, the review is organized in five sections. The first part (in the following) sets an introductory frame and an edition and context. The second part covers synthetic aspect with emphasis on conventional as well as novel reaction schemes utilized to synthesise hydrazine derivatives. The third section of this chapter provides an overview of the analytical methods used in this field for the characterisation of these compounds, with an emphasis on structure, purity and stereochemistry. The fourth part discusses applications and structure–activity relationship in real life, along with conclusions, limitations and future works in the fifth part.

Synthetic Methodologies of Hydrazine Derivatives

This is because the hydrazine moiety can serve as a building block of various nitrogen containing compounds, hydrazine derivatives occupy an indispensable position in nitrogen chemistry. Such derivatives, including hydrazones, azines, acylhydrazides, and heterocyclic analogs, are also prepared through a number of classical and newer methods. Each synthetic strategy is designed based on the position of the substitution, the electronic nature as well as the application for which is intended, medicinal chemistry in combination with material science. In recent decades great advances have been made in the search for convenient, sustainable, and scalable synthetic routes towards meeting contemporary requirements either for research or industry.

Among the oldest and one of the most commonly used methods of preparing hydrazine derivatives is that of the condensation of hydrazine or substituted hydrazines with carbonyl-containing substrates, e.g. aldehydes and/or ketones. This reaction leads to the generation of hydrazones or azines, depending on the stoichiometry and reactivity. These condensation reactions are generally performed under reflux in ethanol or methanol and very frequently do not require a catalyst. However, the regioselectivity and the yield of these reactions may be difficult to control, especially when using asymmetrical carbonyl compounds.

Another widely investigated synthetic path is the acylation of hydrazine with acid chlorides, anhydrides, esters, resulting in the preparation of acylhydrazides. The interest of these compounds in drug discovery is also

justified by their potential use as building blocks of heterocycles. Dehydrative or oxidative cyclization of acylhydrazides gives access to pyrazoles, triazoles and other nitrogen-containing moieties. These transformations are important for the construction of numerous bioactive scaffolds.

In the wake of these recent events, one-pot and multi-component reactions (MCRs) for preparation of hydrazine derivatives have been developed. These reactions have great advantages with respect to atom economy, retardation of the reaction times, and a reduction in the amount of solvent used. For example, the one-pot method using reaction of aldehyde, hydrazines and acid chlorides can result in the highly yielding, corresponding hydrazides and hydrazones without isolation of intermediates. These strategies are particularly well-suited for combinatorial chemistry and high-throughput screening efforts and are thus attractive for the fast library synthesis in a medicinal chemistry campaign.

With the increasing attention on sustainable chemistry, there is a renewed interest in greener methods for synthesizing hydrazine derivatives. Solvent free reactions, ionic liquids, and water reactions have been used to reduce the environmental impact of chemical synthesis. For instance, solvent free grinding approach of hydrazine hydrate with aromatic aldehydes afforded hydrazones in good to excellent yield with lowest energy. Similarly, the reactions become faster and product purity is improved (due to the fact that the side reactions decrease) by using biodegradable ionic liquids as reaction media.

Microwave induced synthesis has also impacted on the field of hydrazine chemistry by providing a means to reduce reaction times and increase yields. The non-equilibrium heating induced by MW irradiation enables accelerated formation of hydrazones as well as hydrazides under much milder conditions. This strategy is very attractive in time-critical synthesis sequences or with intermediates which are easily decomposed. The ultrasound-assisted synthesis provides these same advantages via the cavitation effects that enhance reagent personality and drive improved reaction rates. Despite the special instrumentation, many of these techniques have become increasingly popular in academic and industrial laboratories.

Hydrazine moieties play an important role among therapeutic drugs and biological active molecules, transition metal-catalyzed strategies have become a prevalent approach for the facile construction of hydrazine-containing skeletons. Pd-, Cu- and Fe-catalyzed cross-coupling reaction of hydrazines with aryl halides: synthesis of arylhydrazines and substituted hydrazones. These methods are key to the discovery of targeted drugs and imageable agents. The Buchwald–Hartwig amination and Chan–Lam coupling represent two prominent cases of hydrazines acting as nucleophilic partners in C–N bond formations. In addition, metal-catalyzed cycloadditions and oxidative annulations of hydrazines can result in the creation of fused heterocycles, including indazoles, pyrazolines, and triazines, that are frequently encountered in biologically active molecules.

One of the most important directions in hydrazine chemistry as of 2020 is the rapid incorporation of flow chemistry for continuous synthesis. Flow reactors allow for the controlled conditions of the reaction, safer use, and for the process to be scaled up. In this connection, hydrazine and its homologues at high rates are being manufactured through flow processes, to produce high-purity products and minimize waste.

A number of new syntheses have appeared in the literature between 2020 and 2025 in the area of regioselective substitution, asymmetric synthesis and the use of green solvents. For instance, eco-friendly solvents (e.g., ethyl lactate, glycerol) have been effectively employed for the preparation of hydrazone-linked heterocycles and other such as pyrimidines. Enzymatic catalysis with hydrazine-tolerant oxidoreductases is being investigated for the development of more sustainable synthetic routes but is also at an early stage.

In summary, the artificial world of hydrazine analogs continues to expand at a fast pace. The design of such materials has become feasible due to a wide range of classical and contemporary synthetic procedures that can be modified to suit particular functional demand. The selection of the method, whether it is for library synthesis for drug development or scale up for industrial application, is influenced by a number of factors including yield,

purity, environmental considerations, reagent availability and so on. Crucially, these synthetic efforts must be coupled to parallel advances in analytical chemistry to validate the identity and purity of products, which will be covered in the next part of this review.

Characterization Techniques

Hydrazine derivatives are a vital target for characterization to determine molecular identity, purity, structural properties and functional group organization. Because hydrazine compounds exhibit such a wide range of structures and function, a variety of analytical means are typically used together to gain an understanding of it. These methodologies serve not only as a proof of the success of the developed synthetic pathway, but also as a way to gain contributions on the reaction mechanism, stereochemistry and reactivity tendencies. From the large number of techniques, nuclear magnetic resonance (NMR) spectroscopy, infrared (IR) spectroscopy, ultraviolet-visible (UV-Vis) spectroscopy, mass spectrometry (MS), elemental analysis and X-ray crystallography are the most commonly employed for hydrazine derivatives.

NMR Spectroscopy NMR spectroscopy has continued to be a powerful tool in the structure elucidation of organic compounds, and hydrazine derivatives are no exception. The proton (^1H NMR) and carbon (^13C NMR) spectra give complete signals of the chemical environments of all of the hydrogen and carbon atoms. For hydrazones and acylhydrazides, characteristic chemical shifts of the NH, N=CH, and aromatic protons can often be resolved. NH protons usually resonate downfield (δ = 8–11 ppm) due to deshielding from neighboring electronegative atoms or hydrogen bonding. The imine proton (N=CH) in hydrazones occurs at δ = 7.5–8.5 ppm. ^13C NMR studies establish the carbonyl and imine carbon environments that typically occur in the δ = 150–180 ppm range. For larger molecules or structures, 2D NMR such as COSY, HSQC, and HMBC are employed for correlation studies, particularly when dealing with overlapping aromatic regions or with heterocyclic fragments. For nitrogen containing derivatives, ^15N NMR, although sensitive demanding, may provide useful insight in terms of electronic density and binding nature at nitrogen centers.

Fourier Transform Infrared (FT-IR) spectroscopy is a key technique for the characterization of functional groups and bonding modes. Hydrazine derivatives typically exhibit two strong NH and NH_2 stretching vibration bands at between 3300–3500 cm⁻1 which are broadened by hydrogen bonding. Imine (C=N) stretching vibration peaks were usually found at 1580-1640 cm^{-1}, and they supported that hydrazine had been successfully condensed with carbonyl compounds. In acylhydrazides, the carbonyl (C=O) stretching is observed as a sharp bands in the range 1650–1750 cm^{-1}. The existence of more peaks due to NO_2, CN or halogen substituted can be helpful for the functionalized derivative differentiation. IR spectroscopy is very handy for fast quality control in a synthetic workflow, while it can also be screened more quickly to NMR.

Ultraviolet-Visible (UV-Vis) Spectroscopy is mainly used for studying the electronic transitions of the conjugated system and many hydrazine derivatives (particulary those having aromatic rings) contain these chromophores. The π–π* transitions occurred at 200–300 nm, and the n–π* transitions, which are characteristic for imine and carbonyl groups, were centered at 300–400 nm. Hydrazones' linkages especially have strong absorbance in the UV region as a result of the extended conjugation, of which the bands can be utilized to the Beer–Lambert law for concentration determination of the compound. It's also essential for kinetically oriented measurements for example reaction progress that you need to follow as well as degradation pathways.

Mass spectrometry (MS) is a useful technique for the molecular weight and fragmentation profiles of hydrazine derivatives. There are several widely used ionization techniques, such as Electron Ionization (EI), Electro-spray Ionization (ESI) and Matrix-Assisted Laser Desorption Ionization (MALDI) which depend on the polarity and molecular size of the analyte to be ionized. Typical fragmentation patterns for hydrazine derivatives are loss of N_2, water, or alkyl groups. The fragment pathways in tandem MS (MS/MS) may be followed to give structural information on substituents and core framework. MS is the key technology to identify the compound, especially

in complex mixtures or crude reaction products, frequently coupled to chromatography (e.g., HPLC and LC-MS).

Elemental analysis To confirm the empirical formula, it is necessary to determine the percentage of the elements — carbon, hydrogen, nitrogen, possibly sulphur and / or halogens (X) — in the composition of the compound. This method is primarily beneficial for newly prepared hydrazine derivatives to reconcile theoretical predictions with experimental results in confirming the molecular composition. For ultra-pure samples, error < 0.4% is typically acceptable and differences will commonly be indicative of remaining solvent or impurities. Elemental analysis is not, strictly speaking, a structural method, but it does verify the stoichiometric validity of a compound and serves as a supplement to other spectroscopic data.

Thermal Analysis Techniques including Thermogravimetric Analysis (TGA) and Differential Scanning Calorimetry (DSC) play an important role in the characterization of the thermal stability, melting points and decomposition profiles of hydrazine derivatives. TGA actually measures the weight loss as a function of temperature, which can help to identify the level of moisture content, residual solvents, other volatile matter, and thermal degradation behavior. DSC can be employed for endothermic and exothermic transitions, useful in the study of polymorphism and in determination of the energetic potential (notably in the case of hydrazine derivative used as propellant, or explosive). Together, these approaches are indispensable for testing the applicability of such compounds under various environmental conditions.

Method of Single-Crystal X-ray Diffraction (SC-XRD) remains the ultimate tool to establish the molecular and crystal structures which not only allows to determine precise atomic coordinates of atoms, and to characterise molecular geometry, bond lengths, angles, and intermolecular interactions. For those hydrazine derivatives capable of crystallization, XRD has been used to disclose not only the hydrogen-bonding network, but also planarity, conformational preferences and stereochemical organization. Lone pairs on nitrogen, π-stacking interactions, and in some cases coordination with metal centers (in the case of complexes) can all be visualized easily. The method, generally used as a final proof once only a tentative structure has been obtained and very much appreciated in the synthetic organic and material chemistry research.

Applications

Hydrazine derivatives are an important and versatile class of compounds that have found numerous applications in medicinal chemistry, agriculture, industry, and material science. Due to their diverse structures and reactivity, iron complexes are commonly used as pharmacophores, chemical intermediates, ligands, and functional materials. This section reviews the principal applications of hydrazine-containing molecules, focusing on the structure-activity relationships (SAR) therapeutic indications, market size and commercial trends.

Medicinal Applications

Medicinal chemistry constitutes one of the major fields for hydrazine derivatives. These chemicals have demonstrated medicinally importance and therapeutic potential because they have a wide range of biological actions. In this view, hydrazones and acylhydrazides have been of great interest and widely studied for their antimicrobial, anticancer, antitubercular, antiviral, anti-inflammatory, and anticonvulsant activities. They have great capacity for hydrogen bonding, metal chelating, and redox reactions which is why they are good candidates to target an array of enzymes and biological receptors.

In the area of antimicrobial Potent in vitro activity against both Gram-positive and Gram-negative bacteria has been reported in many studies. Antibacterial activity is favored through the introduction of derivatives bearing electron-withdrawing substituents, such as nitro or halogens, on the aromatic rings. There are also antifungal hydrazones that have been synthesized, which are active on Candida albicans and Aspergillus species.

In oncology, agents like isoniazid hydrazones and thiosemicarbazone derivatives demonstrated cytotoxic activity against a series of human cancer cell lines, such as MCF-7 (breast), A549 (lung), and HT-29 (colon) carcinoma cells. The postulated mechanism is frequently based on the chelation of intracellular iron that ultimately results in the inactivation of ribonucleotide reductase and apoptosis. Certain derivatives also function as kinase and/or DNA intercalator blockers, affecting the cell proliferation path ways.

Hydrazine derivatives are also used to treat tuberculosis. Isoniazid is an old and potent anti-TB drug that is a member of the hydrazide chemical family, which is a synthetic, derivative of hydrazine, and inhibits M. tuberculosis by blocking the formation of the mycobacterial cell wall. More recent derivatizations from this scaffold had produced a new class of antitubercular agents active against resistant strains.

Agricultural Applications

Hydrazine-containing compounds are also employed in agriculture as herbicides, insecticides, and plant growth regulators. Some commercial agrochemicals having hydrazide and hypdrazone groups function to block the enzymatic or hormonal pathways in the pests or plants It is interesting to note that certain commercial agrochemicals have hydrazide and hydrazone groups on the molecule which serve to interrupt the enzymatic or hormonal pathway in the pests or plants.

For instance, maleic hydrazide is a well known plant growth inhibitor which inhibits sprouting of onions and potatoes during storage. It acts by being capable of interfering with auxin-sensitive growth control. Similarly, certain of the hydrazone derivatives are effective insecticides, for example, in that they inhibit neural transmission in the pest or serve as antifeedants. Their selectivity and low mammalian toxicity, make them attractive for their use in sustainable agriculture.

Industrial Applications

The hydrazine derivatives are also important industrially as reducing agents, corrosion inhibitors, polymer crosslinking agents and foaming compounds. Azodicarbonamide, a hydrazine derivative, is used as the blowing agent in plastics and rubbers; upon heating, it decomposes to form nitrogen gas, which is what makes the materials foam up into a lightweight and spongy form.

Hydrazine hydrate as well as its derivatives are widely used within boiler water treatment systems as oxygen scavenger to avoid corrosion. These compounds combine with dissolved oxygen to produce non-reactive nitrogen gas and water, preventing the surface of metals from being oxidized. Moreover, substituted hydrazides have been used as curing agents for epoxy resins and adhesives since they possess bifunctional reactivity, and are thermally stable.

Energetic Materials and Propellants

Hydrazine and its chemically-methylated analogs that include monomethylhydrazine (MMH) and unsymmetrical dimethylhydrazine (UDMH), are widely employed in aerospace and defense applications as high energy rocket propellants. This can be attributed to their high enthalpy of decomposition and low ignition delay. Nevertheless, they are also highly toxic and volatile, and so it is desirable to develop safer and environmentally friendly alternatives.

Hydrazine derivatives containing energetic nitro or azido subunits have also been considered as prospective energetic propellants and explosives. Such materials often exhibit enhanced thermal stability and detonation performance, although at the expense of increasingly complicated syntheses and hazardous implications.

Structure–activity relationship (SAR) and lead optimization

SAR of hydrazine derivatives is critically dependent on the nature and position of substitution on the aromatic/aliphatic skeleton. EDGs can also have the effect of modulation of lipophilicity and membrane permeability, whereas, EWGs had the ability to improve binding affinity by means of hydrogen bonding and electrostatic interactions. The geometry of the hydrazone or acylhydrazide bond is also crucial for target recognition.

In drug discovery process compounds undergo lead optimization where these groups are modified to gain favorable pharmacokinetic and pharmacodynamic parameters. Hybrid compounds, which present a combination between hydrazone core and quinoline, thiazole or benzimidazole scaffolds, exhibited higher bioactivity. Structure based in silico docking and QSAR (Quantitative Structure–Activity Relationship) models are being employed preliminarily to predict and validate these interactions before synthesis.

Conclusion

Due to their characteristic structural features and their high chemical reactivity, hydrazine derivatives have widely been recognized as one of the important classes of compounds in current synthetic and applied chemistry. The nucleophilic character of diazine moiety affords these compounds as valuable intermediates for the synthesis of several heterocyclic systems and functionalized molecules. They have applications in a range of areas, e.g. pharmaceuticals, agriculture, industrial manufacturing and energetic materials.

The most recent progress during recent years (from 2020 to 2025) indicates the increasing concern to realize the efficient synthesis and application of hydrazine derivatives. The shift from conventional condensation approaches to higher-yielding, safer alternatives (including microwave- and solvent-free reactions) is motivated by the search of a variation on the classical way to reduce waste. Catalyzed one-pot, one-metal methods have also encouraged the development of more efficient and complex structures. However, even in these cases issues, including scale-up, reproducibility, and safety of some hydrazine-based intermediates remain challenges.

Just as important is the accurate description of these compounds, for which methods such as NMR, FT-IR, UV-Vis spectroscopy, and X-ray crystallography have proved instrumental. Without such powerful structural models, the translation of advances in synthesis to useful, application-ready materials would be greatly impeded.

The field as it stands today is therefore mature, but young or evolving. The presented body of work reviewed here emphasises a strong base for further and new development, while also highlighting the need for further innovation, especially on sustainability, biological safety and advanced molecular design.

6.Future Perspectives

In the longer-term, hydrazine derivatives are expected to represent a strong potential for innovation in both academic and industrial perspectives. A major challenge is the development of sustainable, environmentally benign methodologies for creating new synthetic compounds. Future studies need to focus on green chemistry methodologies including aqueous phase synthesis, enzyme-catalysed transformations and solvothermal conditions. Such methods will not only lessen ecological impact, but furnish cheaper production operations that are scalable and amenable commercialization.

Nanotechnology presents another promising frontier. Nanoscale: Hydrazines Besides simply being used in drug candidate material, hydrazine-containing ligands might be incorporated into nanocarriers for targeted drug delivery, especially in the therapeutic areas of oncology and infectious diseases. Similarly, preparation of hybrid hydrazine materials for energy storage, catalysis, and controlled release systems could potentially yield novel industrial applications.

On the analytic side, real time, high throughput characterisation tools, including in situ spectroscopies and automated reaction monitoring, will provide deep insights into dynamic concepts in hydrazine chemistry. The application of AI and machine learning into predictive synthesis and structure-activity modeling also looks set to transform the way in which novel hydrazine derivatives are designed and optimized.

In addition, regulatory and SDGs could steer research priorities focusing on the safety, eco-responsible and accessibility of these compounds. Now, with emerging global health and industrial problems for which there currently are no effective means of resolution, hydrazine derivatives are in the right place at the right time to make a paradigm-shifting difference via focused innovation.

In general, the development trend of hydrazine chemistry is the combination of the interdiscipline and the technology intersection. Adoption of these routes will deliver continued growth and important societal contributions from this essential class of molecules.

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