Malaysian Catalysis-An International Journal

Malay. Catal.Int.J Vol 2, Issue 1 (2022) 32-47

OVERVIEW

1,3,4-Thiadiazole and Its Derivatives: An Overview on Crystal Structure and Tribology Activities

Received 02th August 2022,
Revised 29th August 2022,
Accepted 29th August 2022

DOI: 10.1039/ mcij.vol2no1.3

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Abstract

1,3,4-Thiadiazole derivatives has been attracted great attention due to application in various areas. Synthesis and crystal structure is briefly investigated. Their application in high temperature and high pressure as anti-friction and antiwear, and improve the anti-wear and extreme pressure properties have been described. The effect of various 1,3,4-thiadiazole additives on the tribological properties of base oils is studied. This paper aims to present an overview of the role of 1,3,4-thiadiazole and its derivative in improving the tribological properties of base oils.

Keywords: 1,3,4- thiadiazole; crystal; anti-corrosion; extreme pressure; tribology

1. Introduction

Over the past five years, interest in heterocyclic compounds such as 1,3,4-thiadiazole and its derivatives has not waned. Searching through journal publication website such as Sciencedirect, Web of Science and Scopus found that it is estimated that more than 300 review articles, 1000 research articles, and more than 100 book chapters have been written by scientists in various research fields, and the most of them related to chemistry with a total of 1056 publications. Hence, it shows that a heterocyclic compound with more than one heteroatom in its ring, such as 1,3,4-thiadiazole has many advantages in the application and chemical structure. Thiadiazole is a five-membered ring containing sulfur and nitrogen atoms with two double bonds, set up an aromatic ring with the molecular formula of $C_2H_2N_2S$. It has four isomers which are 1,2,3-thiadiazole (**1**), 1,2,4-thiadiazole (**2**), 1,2,5-thiadiazole (**3**) and 1,3,4-thiadiazole (**4**) as shown in Figure 1.

Monocyclic azoles are numbered starting with the lowest atomic weight and highest group of heterocyclic atoms in the periodic table.

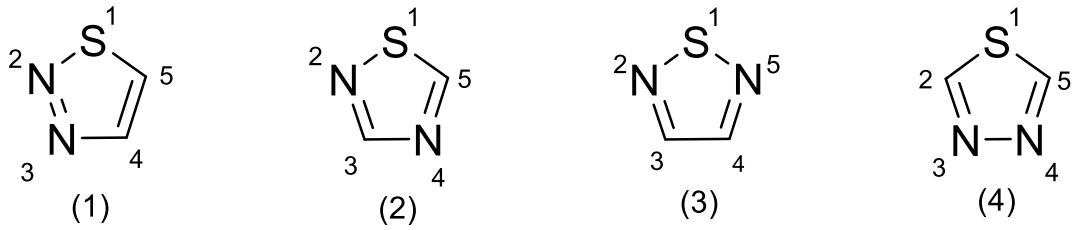


Figure 1: Isomers of thiadiazole

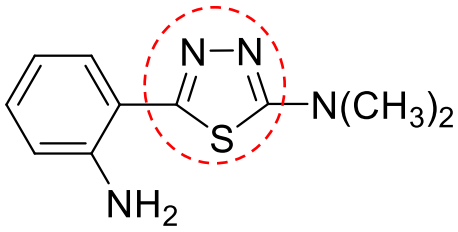
2. The advantages of 1,3,4-thiadiazole

A survey of universal reference literature reveals that 1,3,4-thiadiazole has received greater attention than other isomers. Because of the inductive influence of the sulphur atom, the 1,3,4-thiadiazole ring is a fairly weak base with very high aromaticity [1–3]. It is relatively stable in aqueous acid solutions, although it can ring cleave in an aqueous base. Furthermore, the ring is shown to be very electron deficient due to the electron-withdrawing effect of the nitrogen atoms, as well as relatively inert toward electrophilic substitution but susceptible to nucleophilic attack, whereas when substitutions are introduced into the 2′ or 5′ positions of this ring, it becomes highly activated and readily reacts to yield diverse derivatives. As a result of these unique characteristics, the derivatives of 1,3,4-thiadiazole are widely employed in medical, agricultural, and materials chemistry. Thiadiazole is also widely employed in optics and electrochemistry due to its electron-deficient nature, high electron-acceptance capacity, and thermal and chemical stability [2]. Furthermore, charge-transporting capacity, photoluminescence, photoconductivity, mesomorphism to form liquid crystals, metal anti-corrosive activity, and other applications are heavily concentrated.

The synthesis of thiadiazole and its derivative frequently generates products in the form of crystal structure. Schatz et al. (2020) [4] reported that among all the four isomers, the conformer of dithiol tautomer of 1,3,4-thiadiazole was identified as the most stable due to occurring a charge transfer in the molecule.

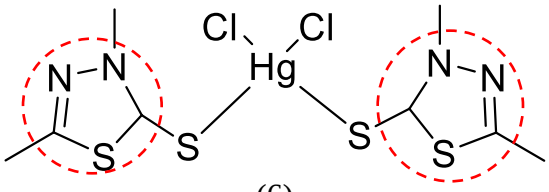
2.1 The study on crystal structure of 1,3,4-thiadiazole

In 2000, [5] confirmed, using X-ray diffraction research, that 3-*N*,*N*-dimethylthioureidoquinazolin-4(3*H*)-one underwent recyclization with the creation of 5-(2'-aminophenyl)-2-dimethylamino-1,3,4-thiadiazole (**5**) using the concentrated sulfuric acid. They discovered that intermolecular hydrogen bonds connected molecules into centrosymmetric dimers that are arranged in flat networks parallel to the *x-y* plane. The crystal structure existed in planar.



(5)

Hu et al. (2010) [6] effectively synthesized two complex structures of 1,3,4-thiadiazole crystal with metal, with yields of 85% and 5%, respectively. X-ray Diffraction analysis of crystals (**6**) and (**7**) revealed that Hg(II) of (**6**) is four coordinated with two chloride anions and two exocyclic sulphur atoms of two adjacent MTDs, and Hg(II) of (**7**) is three coordinated with one chloride anion, one nitrogen atom, and one exocyclic sulphur atom of two adjacent MTDs. By facilitating the intermolecular works between molecules such as S…S and S…Cl for **6** or Hg…S for **7** interactions, both two complexes **6** and **7** are developed in 2D supramolecular architectures.



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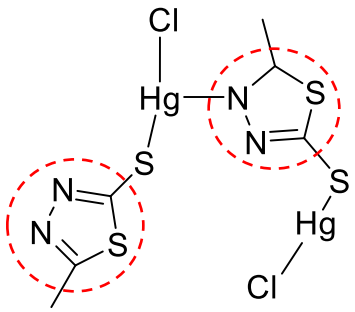
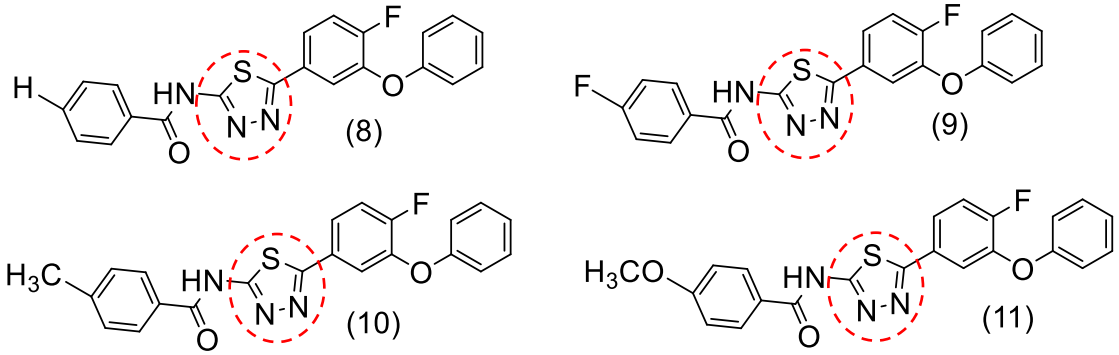


(7)

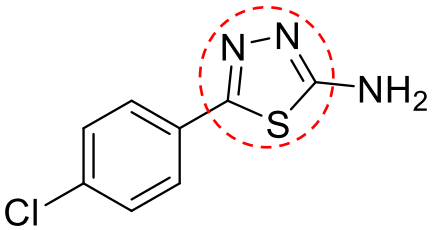
Panini et al. (2013) [7] synthesized a series of 2-benzamido-5-(4-fluoro-3-phenoxyphenyl)-1,3,4-thiadiazoles (**8-11**) with systematically varying functional groups at the para position of the benzamido ring and examined their crystal structures. In addition to the presence of strong N–H–N hydrogen bonds, they discovered that the weak interactions, such as C–H…OLC/O–C, C–H…π, C–H…F, lp…π, π…π play a substantial role in stabilizing the crystal packing.

They found that the weak interactions, such as C–H…OLC/O–C, C–H…π, C–H…F, lp…π, π…π are significant contributors in the stabilization of the crystal packing in addition to the presence of strong N–H…N hydrogen bonds. They were discovered to be not only responsible for the change in crystal structures but also to give extra stability in the absence of any structural change.



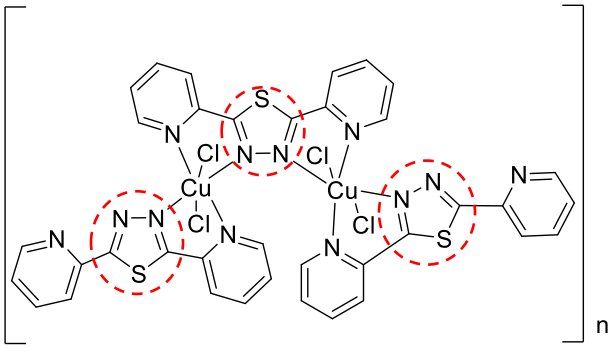
(8-11)

Realizing the wide ranging applications of 2-amino-1,3,4-thiadiazole scaffold and in extension to develop various biologically active conjugates, [8] compared experimental and theoretical (DFT) data of 5-(4-chlorophenyl)-2-amino-1,3,4-thiadiazole (**12**), a molecule with anti-proliferative activity. Based on the comparative analysis between experimental and theoretical data, it it was concluded that NH...N hydrogen bonding and strong conjugative interactions are present in the molecular system, and that the polarization of the molecule increases as a result of the transfer of the π-electron cloud from the donor to the acceptor.



(12)

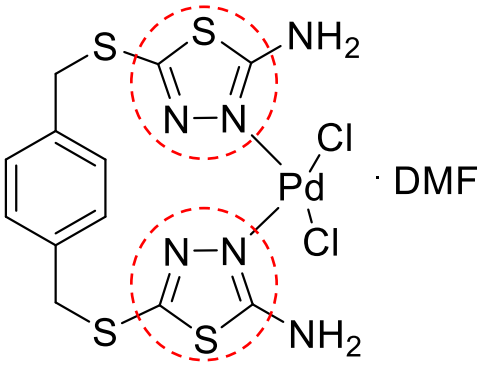
In 2020, [9] synthesized a new copper (II) mono-dimensional coordination polymer based on 2,5-bis(pyridine-2-yl)-1,3,4- thiadiazole using copper salt ($CuCl_2.2H_2O$). The reaction resulted in a crystalline product with structure **13**. They found that the copper cation has an elongated octahedral coordination geometry, with the nitrogen atoms of two 2,5-bis(pyridin-2-yl)1,3,4-thiadiazole ligands occupying the equatorial positions and the chlorine atoms occupying the axial positions. They also found that the crystal cohesion is assured by intermolecular hydrogen bonding, C-H/Cl and π---π stacking between pyridyl and thiadiazole rings forming a three-dimensional structure. They anticipated this newly synthesised polymeric complex to be particularly successful in preventing the in vitro growth of two fungal diseases that affect olive and melon crops.



$[CuLCl_2]_n$

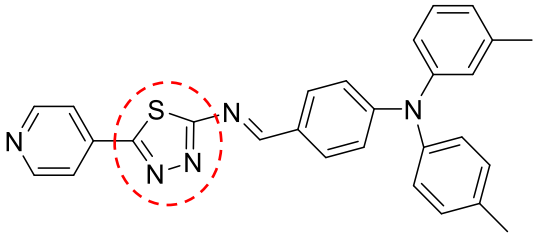
(13)

Meanwhile, [10] synthesized a novel palladium(II) complex containing dipodal bis-1,3,4-thiadiazole-based ligands **14** with the ligands coordinates to the palladium(II) chloride moiety via nitrogen atoms (N2 and N5) of the two heterocycles in *cis* position. The screening of this product against two bacterial pathogens, Staphylococcus aureus and Escherichia coli as well as human colon cancer cell lines (HCT-116) revealed that the cancer cell line viability of this product was dose-dependent and demonstrated cytotoxic activity against the tested cell lines lower than cisplatin, while exhibiting very high to excellent antibacterial activities.



(14)

In 2021, [11] successfully obtained a novel crystal of unsymmetrical imine (**15**) *via* the condensation reaction of 4-(di-p-tolylamino) benzaldehyde and 2-amino-5-(4-pyridinyl)-1,3,4-thiadiazole. The study confirmed the monoclinic crystallisation of the imine, which is stabilised by intermolecular CH... N hydrogen bonds. This CSA-doped imine also shown promise for application in optoelectronics due to its ability to minimise heating caused by current flow and give a complementary absorption spectrum to those typically used.



(15)

3. Synthesis and Application of 1,3,4-thiadiazole Derivatives

3.1 Introduction to lubricant and additives

In general, lubricants' primary role is to reduce wear and friction in moving machinery, as well as to preserve metal surfaces from oxidation. Due to stronger environmental controls, lubricant formulations with much lower or zero phosphorus content are required. It is also preferable for economic reasons that the additive have other functional features that improve the lubricating capabilities of the oil. Different lubricating oils with specific additives formulation were introduced for different applications thus improving the limitations of the base oil. For example, by varying grinding oils on test gears, [12] investigated the effect of grinding oil on the properties of boundary layers and the subsequent gear running behavior. As a result, the finding demonstrates that the surface material attributes differ from the base oil in terms of microstructure. Other than

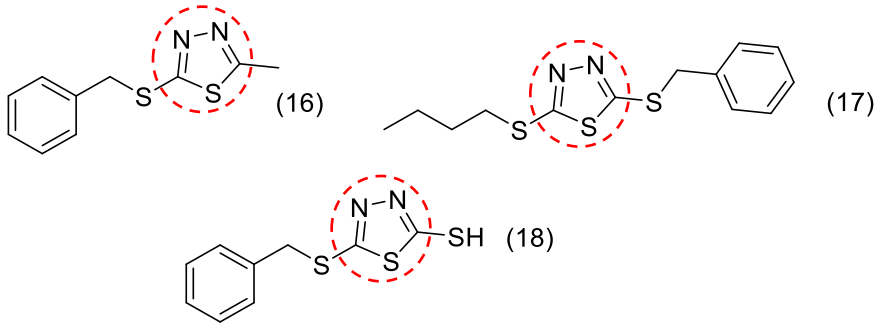
that, [13] utilized grease type of lubricant formulated with molybdenum disulfide (MoS_2) for the loaded rolling bearing. The findings revealed that wear is heavily influenced by loading parameters. MoS_2 greases are thought to perform poorly under constant load, and a lower MoS_2 concentration is thought to provide the same better wear characteristics under varying loads and speeds for extreme pressure applications. In addition, [14] evaluated the influence of lubricant oil composition and the interaction of lubricant additives with fatigue fractures on gear rolling contact fatigue. The sulfur in the extreme pressure (EP) additives, according to the findings, encourages the development of iron sulfide (FeS) at the crack tip, giving a beneficial effect on limiting damage propagation.

3.1 Advantages of 1,3,4-thiadiazole as corrosion inhibitors

Referring to [15], dimercapto-1,3,4-thiadiazole (DMTD) adducts of mercaptan have been studied extensively since the 1950s. These additives are mainly used as a copper corrosion inhibitor and the research into their tribological properties is limited. As stated by [16] , metals can be protected from corrosion by using organic compounds containing heteroatoms with high electron density, such as phosphorus, sulphur, nitrogen, or oxygen, or those containing multiple bonds that can be adsorbed onto the metal surface via electron transfer from the adsorbed species to the vacant d orbital in the metal to form a coordinate type link. Some of these organic compounds demonstrated exceptional inhibitory capacity in different media; they included 1,3,4-thiadiazole (C=N) and its derivatives with amino, thio, hydroxyl, phenyl, alkyl, and some heterocyclic substituents. Thiadiazole derivatives are thought to form a protective film on copper, silver, mild steel, bronze, brass, and cobalt by combining the donor behaviour of the heteroatoms (such as N atoms and S atoms) bearing the lone pair of electrons and the extensively delocalized electrons of the thiadiazole derivative molecules with the acceptor behaviour of the vacant d orbitals of metal surface atoms.

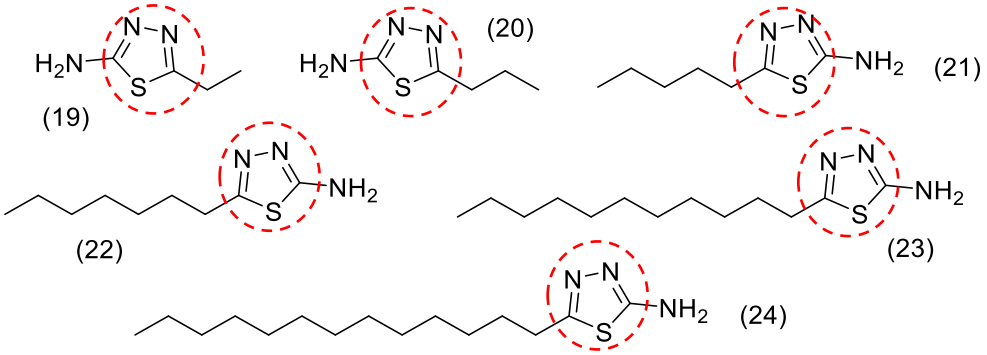
In 2020, [17] produced article on synthesis and evaluates three thiadiazole derivatives (**16-18**) with varying substituent groups as corrosion inhibitors for N80 carbon steel in CO_2-saturated oilfield generated water. As shown by electrochemical studies, the synthesized thiadiazole derivatives have the potential to inhibit the corrosion of N80 carbon steel through chemisorption, with the inhibition efficiency increase in the order **18** > **17** > **16**. The discovered thiadiazole compounds act as mixed-type inhibitors with high anodic efficiency. The Langmuir adsorption isotherm consistently describes their adsorption behavior. The theoretical calculations show that the

synthesized thiadiazole derivatives adsorb on the Fe surface by binding the S atom to the Fe surface atom. The tautomeric shift from thiol-**18** to thione-**18** may account for the compound's potent inhibitory activity.



(16-18)

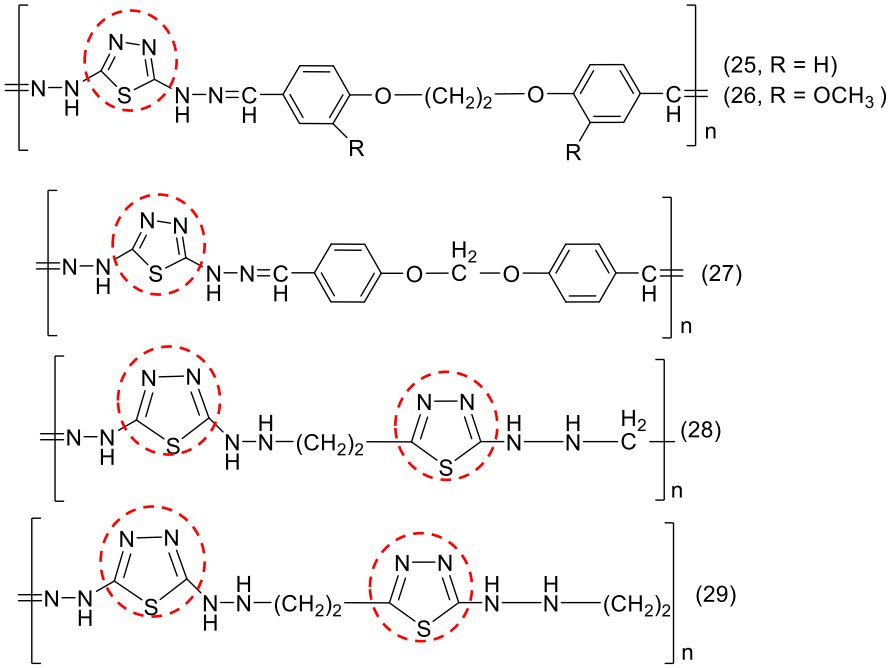
Mi et al. (2020) [18] conducts a theoretical evaluation of the corrosion inhibition performance of six thiadiazole derivatives (**19-24**) by combining quantum chemistry, molecular mechanics, and molecular dynamics simulation approaches. According to the findings, the length of the alkyl chain has little effect on the reactivity of thiadiazole inhibitor molecules. Furthermore, molecular mechanics calculations reveal that a molecule with an elongated alkyl chain can build a self-assembled membrane with improved stability and coverage rate to prevent corrosive chemicals from diffusing to the metal surface.



(19-24)

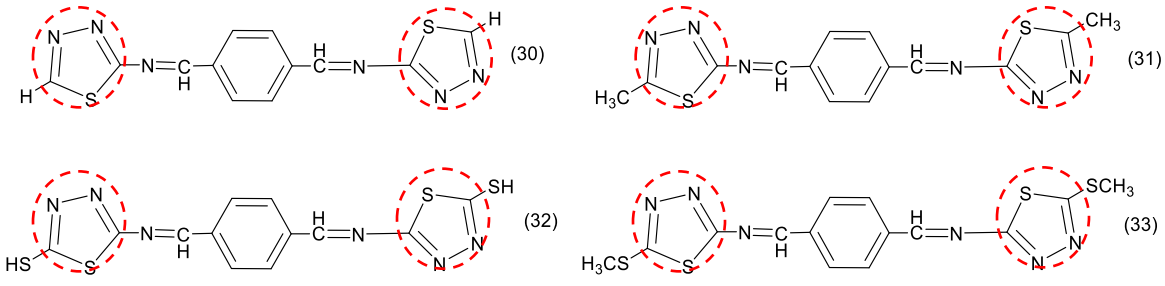
Jassim et al. (2020) [19] successfully synthesized a series of polymers that contain sulfur - heterocyclic ring with a thiadiazole base (**25-29**) and evaluated their properties toward corrosion of tap water. The anti-corrosion polymer was made in two stages, first stage was synthesis of thiadiazole base and continue to second stage with the addition of the polymer into the thiadiazole produced in first stage. From the result of weight loss, the as-produced polymers successfully cover

the surface of the sample and protected them from corrosion, thus exhibit the properties of anti-corrosion.



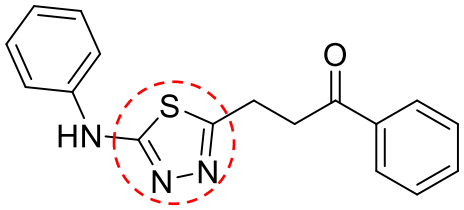
(25-29)

In 2020, [20] published a comparative study that included experimental, theoretical, and surface studies of the corrosion prevention properties of four thiadiazole-derived bis-Schiff bases (**30-33**) for mild steel in strong acidic media. Based on the findings, they concluded that all of the synthesised thiadiazole bis-Schiff base derivatives efficiently resisted mild steel corrosion in strong acidic medium. The inhibitors also worked in a mixed-type mode with surface data revealing the presence of an inhibitor protective barrier on the steel surface, limiting corrosion activities.



(30-33)

Also with the interest of corrosion inhibitor for mild steel in strong acidic medium, [21] reported an experimental investigation employing 1-(Phenylamino-1,3,4-thiadiazol-5-yl)-3-phenyl-3-oxopropan (**34**) as corrosion inhibitor. As a result, **34** showed considerable inhibitive efficacy with the chemisorption adsorption mechanism. They concluded that the as-obtained protection by **34** is mostly provided by the heteroatoms in the inhibitor molecules that represent the adsorption sites. Also, the aromatic rings strengthen the electrostatic contact between the **34** molecules and the mild steel surface. They also discovered that the selected corrosion inhibitor was adsorbed on the mild steel surface, forming a protective barrier against the acidic solution.



(34)

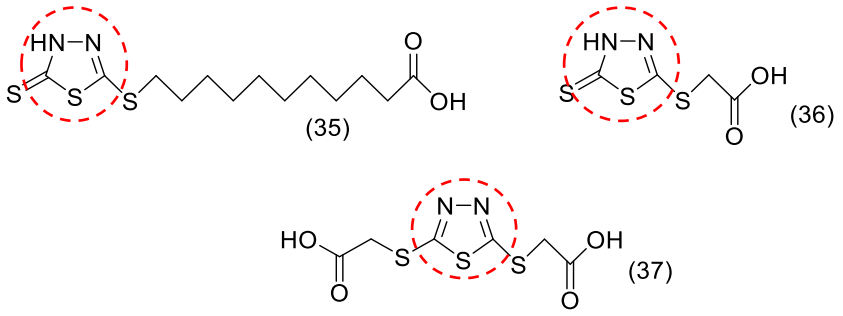
3.2 Advantages of 1,3,4-thiadiazole as multifunctional additives

According to [22], due to the high sulfur content of 2,5-dimercapto-1,3,4-thiadiazole (DMTD), its derivatives may be useful as an extreme pressure additive. Furthermore, DMTD can work as an extreme pressure agent, metal deactivator, metal passivator, or antioxidant according to its unique structure, which provides these capabilities. In addition, [2] highlighted that since 1,3,4-thiadiazole derivatives have outstanding load-carrying, extreme pressure (EP), antiwear (AW), and friction-reducing properties, they are used as lubricant additives in lubricants such rapeseed oil (RSO) and ester-based lubricants. Theoretically, these characteristics would result from the reaction of S atoms with the metal surface and the absorption of N atoms and other heteroatoms (such as the P atom) onto the metal surface to generate a thin chemical protective layer. Additionally, chelation of the N atom's lone pair electrons with the iron surface helps to reduce S corrosion.

Furthermore, [23] in 2012 stated that as most DMTD are insoluble in common base oil, so their derivatives with certain functional groups are designed for the purpose of enhancing their oil solubility.

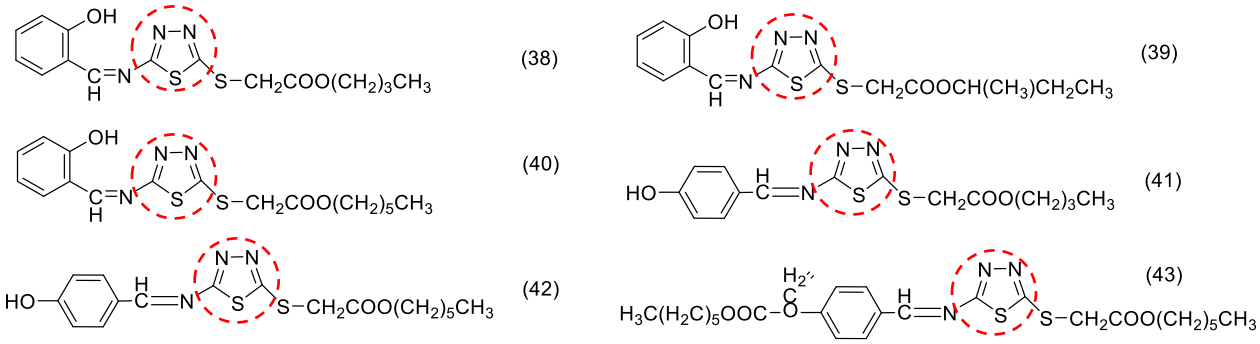
Wang et al. (2014) [24] synthesized three 2,5-dimercapto-1,3,4-thiadiazole derivatives (**35-37**). Their tribological, anticorrosion, and antirust as water-soluble additives in water– glycol hydraulic

fluid were investigated. All the synthesized DMTD derivatives were shown to have high solubility in the base liquid, which significantly enhanced the liquid's extreme pressure, antiwear, and friction-reducing capabilities. It has been hypothesized that the EP, antiwear, and friction-reducing capabilities of additive **35** are mostly attributable to the development of a protective layer through chemical adsorption of its long-chain alkyl carboxyl group. Under normal tribological conditions, **36** and **37** primarily create a protective film through the complexation of the 1,3,4-thiadiazole ring with the metal surface. In addition, the antiwear and friction-reducing capabilities of the base liquid were also greatly enhanced by the chemical adsorption of the alkyl carboxyl group on the metal surface. However, in highly severe conditions, the EP performance of the base liquid is considerably improved when additives **36** and **37** disintegrate into small sulfur-containing molecules and interact further with the metal surface to generate an efficient EP coating.



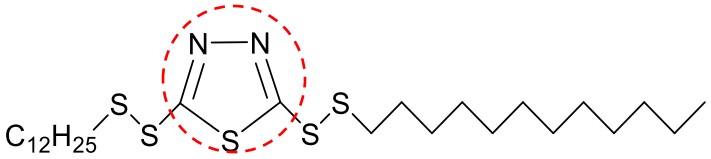
(35-37)

Shen et al. (2017) [25] synthesised a new series of 1,3,4-thiadiazole Schiff base derivatives (**38-43**), and studied their anti-corrosion, thermal stability, and tribology properties. Their findings showed that the thiadiazole Schiff base derivatives had good thermal stability, corrosion resistance, and they remarkably improved the tribological properties of the base oil. It was proposed that during the friction process, the adsorbed additives reacted with the steel surfaces, resulting in the formation of a protective coating constituted of sulphates, sulphides, and organic nitrogen compounds. They further speculated that these synthetic additives could find use in the engine oil and rolling bearing industries.



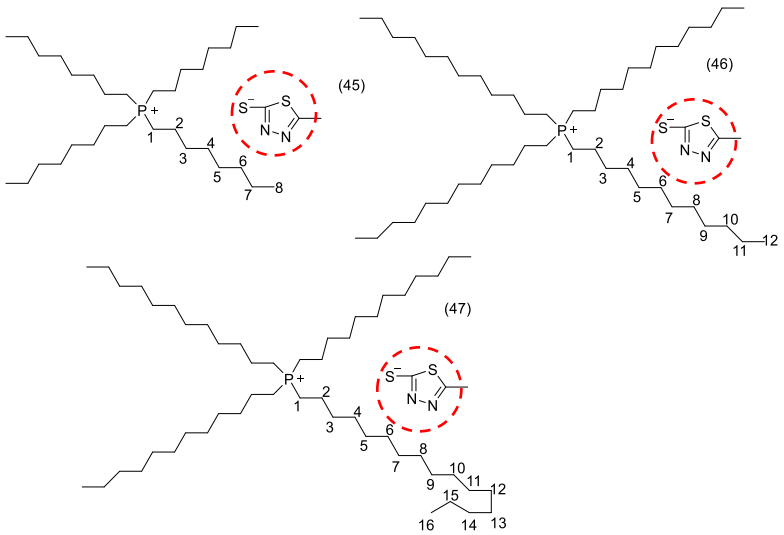
(38-43)

Tan et al. (2018) [26] investigated the tribology properties of over-based calcium or magnesium sulfonate compounded with 2,5-bis(dodecyldisulfanyl)-1,3,4-thiadiazole (**44**) in rapeseed oil. Both additives possessed good load-carrying capacity and showed excellent antiwear and friction-reducing of oil. In order to protective film formation, it was found that both additives could promote the decomposition of thiadiazole, and more active sulphur would be released to form $CaSO_4$ ($MgSO_4$), which contributed to improve the tribological performance of the lubricant.



(44)

Ionic liquids (ILs) have high stability and cause less friction. Different ILs have varying molecular structures and lubricating characteristics. The use of ILs as boundary lubricants is becoming increasingly appealing due to their strong heat stability and good tribological qualities. Recently in 2022, [27] synthesized three ionic liquids based on 2-mercapto-5-methyl-1,3,4-thiadiazole (MMT) (**45-47**) and assessed their tribological performance using friction tests and worn surface studies. According to the results, the synthesized MMT-based ILs shown astonishing corrosion inhibition efficiencies. MMT functionalized ILs outperformed conventional ILs regarding friction reduction and anti-wear performance. The ILs adsorption layer and tribo-film, constituted of iron oxide, ferrous disulfide, and ILs decomposition products, were found to be responsible for the outstanding lubricating performance of MMT functionalized ILs using worn surface studies.



(45-47)

4. Future outlooks

We can infer from this review that, despite having numerous advantages and being generated as crystal with some derivatives, the sulfur and nitrogen-containing heterocyclic additives, such as 1,3,4-thiadiazole also exhibit a beneficial influence when added with metalworking fluids. Design and synthesis new thiadiazole derivatives and study their solubility and EP and AW performance in base oils is an interesting topic for the research. In addition, more research into the molecular and atomic features of thiadiazole mechanisms is needed in the future.

Conflicts of interest

The author declares that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

The authors used a Research grant IIRG 004A-2022 FNW from the Ministry of Higher Education (MOHE), Malaysia, to conduct this work.

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