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Chemical properties of thiadiazole compounds

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Abstract:

Heterocyclic compounds occur widely in nature and in a variety of non-naturally compounds, large number of heterocyclic compounds are essential to life such as alkaloids, antibiotics, essential amino acids, the vitamins, hemoglobin, hormones , a large number of synthetic drugs and dyes. Thiadiazole are very interesting compounds due to their important applications in many pharmaceutical biological and analytical fields. This review showed the optical , electrochemical properties , electrical conductivity and magnetic susceptibility for thiadiazole compounds .

Keywords : Heterocyclic compounds , thiadiazole compounds , chemical properties .

1-1: Heterocyclic Compounds :

A Heterocyclic are compounds with at least structure of one ring and a non-carbon atom.[1] The first series of heterocyclic compounds are three-member ring heterocycles containing single atoms of either, (O) (oxiridine) or (S) (thiirane) , (N) (azirine) in Figure (1- 1) (a). The four-member ring is observed in heterocyclic. The using of compounds as antibiotics such as cephalosporins and penicillin. Common examples are azetidine and dithiete in Figure (1) (b). Thietanes are used as fungicides and bactericides and also using in the production of polymers and inhibit iron corrosion [2]. The five-membered ring family represents an main segment of the heterocycles consisting of indoles, proline and hydroxyproline, which is a major constituent of collagen. The heme group related to myoglobin, hemoglobin and chlorophylls are all formed from Thiophene , furan and the pyrrole units of porphyrin in Figure (1)(c) are examples of five membered heterocycles containing sulfur and oxygen respectively.[2] As the size of ring increases, the number of derivatives increases because of varying the location possibility of the heteroatoms in the structures of the molecular. This research will make most use of the five-membered ring to benzene ring.

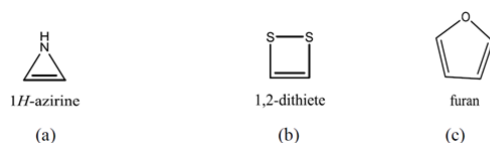


Figure (1-1) Examples of heterogeneous ring compounds

1-2.Thiadiazole compounds :

Thiadiazole is an main five heterocyclic ring compounds that containing two nitrogen atoms and one Sulphur atom. Thiadiazoles are an main type of heterocyclic compounds that exhibit diverse applications in organic induction, pharmaceutical and biological applications. They also known to useful as oxidation inhibitors, cyanine dyes, metal chelating agents, anti-corrosion agents[3][4]There are four isomeric classes depending on the situation of nitrogen atoms to each other : 1,2,3-thiadiazole; 1,3,4-thiadiazole; 1,2,4-thiadiazole and 1,2,5-thiadiazole as in the figure (1-2) [5].

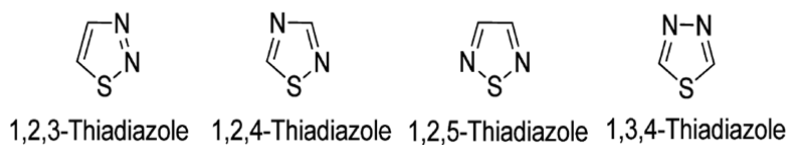


Figure (1-2) Isomers for thiadiazole compound

The curative importance of these rings prompted us to develop eclectic molecules in which a change could be considered in a pharmacological activity[6][7].

1-2-1. Important in Chemistry :

Thiadiazole showed entertaining optical, electronic, and chemical properties. It had been studied as an elegant candidate for organic bridging ligands to heteroatoms, N and S, with free electron pairs could device active coordination positions for metal ions or/and hydrogen-bond acceptors to expand polymeric frameworks. Moreover, introduction of amino/mercapto/hydroxyl substituents possessing tautomeric ability as well as some other common metal chelating ligands (such as phenyl, pyridyl[8][9], thiophene, etc.) can extend thiadiazole's approach into structure coordination chemistry. With the presence of conjugated π systems and the electron transfer between heteroatoms 31 (mainly N, S) and metal, the polymeric metal-organic frameworks with a thiadiazole component exhibited potential applications in catalysis, luminescence, magnetism, sorption, ion exchange, nonlinear optics, electricity, etc.[10][11].

1-2-1-A. Optical Importance :

The derivative of thiadiazole containing synthesized vinyl, and their polymers which can emit heavy blue or green fluorescence have good solubility in CHCl_3 or DMF.[12] The compounds coordination for transition metals with a 2,5-(R) thiadiazole derivative as the ligand exhibited a two-dimensional framework which further assembled into a three-dimensional supramolecular network via interlayer π - π -stacking interactions and strong hydrogen bonds, showing emitting blue photoluminescence in the solid state at room temperature[13]. Photo induced intermolecular charge transfer, the key to photoluminescence, needed a molecular assembly containing electron-donor units and electron-accepting units as well as an intermolecular π -conjugated structure. The aromatic thiadiazole ring derivative allows good π -electron conjugation and was demonstrated as a good candidate for its electron-withdrawing property[14-16]. It was also hypothesized that the luminance emission of the metal-thiadiazole network might be attributable to the intraligand transitions modulated by metal coordination and/or ligand-to-metal charge transfer (LMCT)[17].

Fluorescent chemosensors with their simplicity, high sensitivity, and fast response time have attracted enormous interest. With thiadiazoles as a fluorophore, the emitted fluorescence can be quenched or enhanced by a metal ion, suggesting that the metal-thiadiazole complexes can be used as metal-ion-selective sensors even via the naked eye detecting modes. In addition, these proposed methods can be tentatively utilized for 32 determination of heavy metal ions in tap water, river water, and industrial wastewater samples[18]. Cu^{2+} complexes derived from unsymmetric thiadiazoles exhibited mesogenic

properties, and an excited-state intramolecular proton transfer (ESIPT) reaction in this type of o-hydroxy thiadiazole was also observed accompanied by the two phototautomer forms, enol and keto, coexisting in the excited state [19].

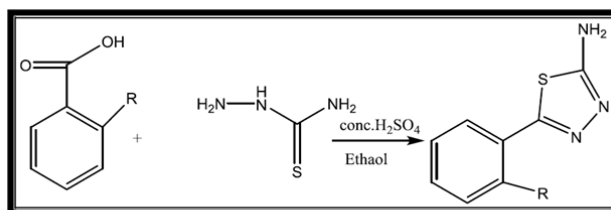
1-2-1-B. Electrochemical Importance :

With phenyl units and thiadiazole rings linked through acetylene groups, a π system extending throughout the molecular structure called a Poly (aryl-ethynylene) (PAE) system was obtained. Polymers involving this system showed rather low intramolecular reorganization energies and can be considered as candidates for n-type semiconductors.[10] 1,3,4-Thiadiazole-dithiolate/disulfide usually showed prototropic tautomerism, acid–base equilibrium, and redox behavior based on a mercapto–disulfido conversion in the assembly reactions with metal ions, which were reportedly used as multidentate linkers or capacitance measurements in semiconductors.[20][21] An amperometric sensor with attractive sensing behavior was prepared using solid carbon paste as substrate for poly(2-amino-5-mercapto-1,3,4-thiadiazole) (AMT, PAMT) film.[22] In addition, the PAMT film was also used for selective determination of L-cysteine and folic acid[23] 2,5-Dimercapto-1,3,4-thiadiazole (DMcT) polymer PDMcT was also used to entrap a great deal of glucose oxidase GOx or tyrosinase and form PDMcT enzyme composites and then coelectro deposited with poly- (DMcT) on an Au electrode, which was demonstrated as sensitive glucose and phenolic biosensors[24]. In the currently decade, organosulfur-based compounds with multiple thiol groups or disulfide moieties have 33.

received attention as potential cathode electro active materials for lithium /lithium ion rechargeable batteries due to their high capacities to release and capture Lithium ions during charge/discharge cycles as well as the advantage of low cost. However, the sluggish kinetics of the redox reactions at room temperature, the lack of electronic conductivity, and the poor charge/discharge durability in liquid electrolyte systems made organo sulfur materials application limited. DMcT was reported as one of the most promising organo sulfur compounds as a cathode active material, and its redox reaction can be accelerated by the high electrocatalytic activity of the conducting polymers poly(3,4-ethylenedioxythiophene) (PEDOT),[24], [25] polypyrrole (Ppy), and polyaniline (PAn).[26], [27] Except for dye-sensitized solar cell, 1,3,4-thiadiazoles were also applied to form thin films of coordination complexes which had particular optical, electrical, magnetic, and catalytic properties.[28] In addition, two new perylene diimide derivatives obtained by functionalizing the basic perylene molecular core at imide nitrogen with thiadiazole rings made possible the fabrication of n-type organic thin-film transistors able to work in air[29].

1-3: Importance of some Thiadiazole Derivatives :

Remarkable progress has been made in the development of thiadiazole derivatives as shown in the equation (1-1) in the recent years and the most recent studies have revealed that thiadiazole derivatives have a wide spectrum of pharmacological properties like, antimicrobial[30],[31] as the compounds shown in the figure (1-3) (a,b). anti-inflammatory[32],[33] such as the compounds shown in the figure (1-4)(a,b), anticancer[34][35] such as the compounds shown in the figure (1- 5) (a,b), antidiabetic activity [35],[36] such as the compounds shown in the figure (1-6) (a,b), antioxidant activity[37][38] anticonvulsant[39][40] such as the compounds shown in the figure (1-7) (a,b). Antitubercular activity[41] such as the compound shown in the figure (1-8) . Nataliya Zelisko *etal.* were syntheses thiopyrano[2,3-d][1,3]thiazole (2) and chromeno[4',3':4,5]thiopyrano[2,3-d]thiazole (3) derivatives [42] , Amal Hussein ,2019, prepared some new derivatives of thiadiazole [1, 4-bis ((2-(5-hydrazineyl-1, 3, 4-thiadiazol-2-yl) hydrazineylidene) methyl) benzene and (2,2'-((1,3,4-thiadiazole-2,5- diyl)bis(sulfanediyl))bis(N-(5-amino-4H-1,2,4-triazol-3-yl)acetamide) [43] .



.....(1-1)

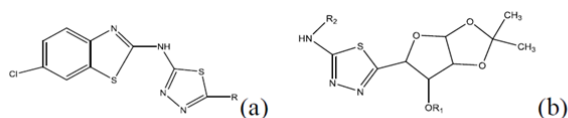


Figure (1-3) examples thiazole derivative biologically effective

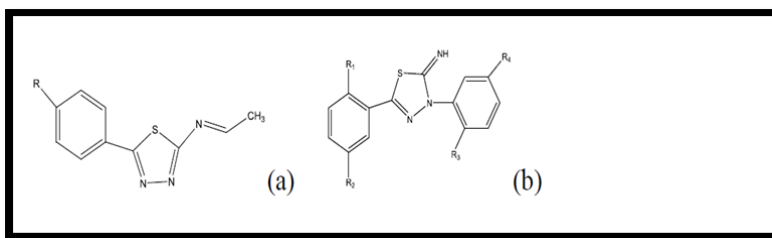


Figure (1-4) examples thiazole derivative anti-inflammatory effective

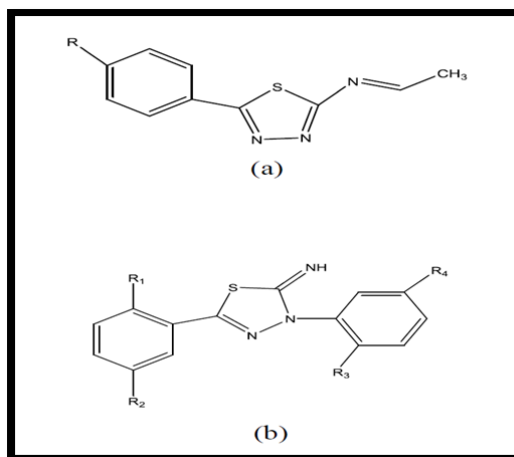


Figure (1-5) examples thiazole derivative anticancer effective

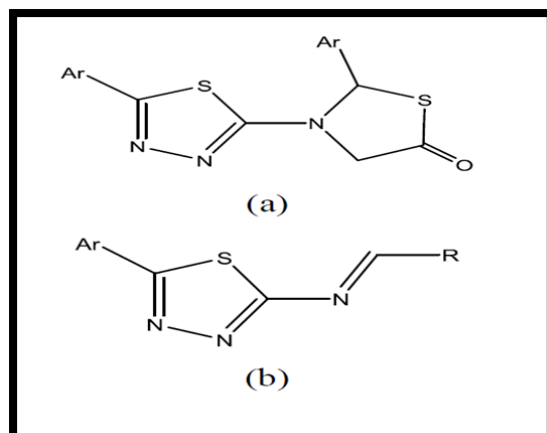


Figure (1-6) examples thiazole derivative antidiabetic activity effective

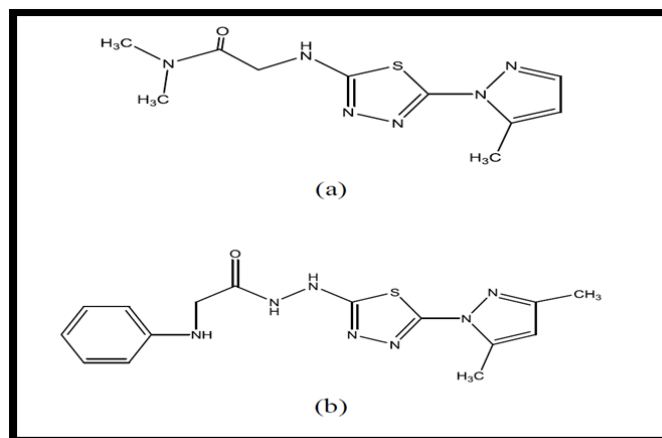


Figure (1-7) examples thiazole derivative (a) antioxidant and (b) anticonvulsant activity

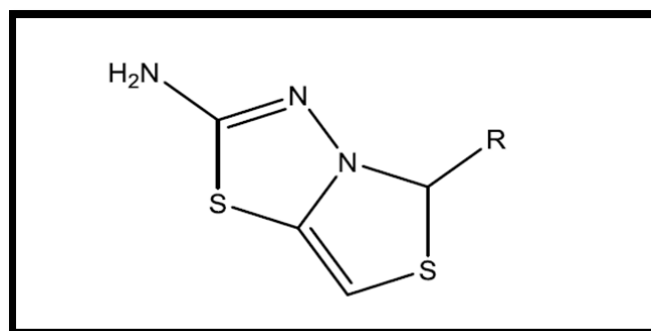


Figure (1-8) examples thiazole derivative Antitubercular effective

1-4: Electrical Accessibility :

Electrical accessibility in solid-phase materials is the process of moving charge carriers within the material under the influence of an electric field. These carriers may be electrons as in solid materials and metals or they are on Form ions as is the case in liquid solutions. In semiconductors conduction is accomplished via pair(Electron - hole) [44]. The organic semiconductor materials include polycyclic aromatic hydrocarbons (PAHs), metal complexes, and small compounds derived from conductive

polymers such as polyacenes, polyphenylamines and polythiophenes [45][46]. Organic semiconductors (OSCs) are known as organic π -conjugated materials with good charge transport and/or electroluminescent properties, and widely used in organic and hybrid electronic devices such as organic light emitting diodes (OLEDs), organic photovoltaic cells (OPVs) and organic field-effect transistors (OFETs)[47][48]. The relationships between molecular and supramolecular structures and the semiconducting properties of these materials have become crucial subjects over the past years; most of them concerning the evaluation of the band gap energy of OSCs[49][50]. In fact, the band gap energy denotes the energy separation between the 51 highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO), the analogues to the valence and conduction bands of the inorganic semiconductors (ISCs), respectively, and the molecular alignment and packing influences the HOMO and LUMO energy levels. The control of HOMO, LUMO energy gap of π -conjugated systems, and hence of the band gap of the corresponding materials, is a critical task for the semiconductor and nanomaterial industries [51][52]. The conducting properties of an OSC are dependent on the energy gap, and it is well-established that the band gap energy of insulators is larger than (>4 eV), but lower for semiconductors (<4 eV). The band-gap energy of organic π -conjugated semiconductors is related with the electronic band structure and depends on the pressure and temperature [53][54]. They tend to decrease with increasing Temperature due to increased atomic vibrations that lead to larger average interatomic spacing. The knowledge of the band gap is a major factor determining the electrical conductivity of a solid. It is of extremely fundamental in organic electronics, being decisive for choosing the OSC material for the manufacturing of stable and efficient Organic Light Emitting Diodes (OLEDs) and Organic Photo Voltaic cells (OPVs). In these electronic devices, the efficiency of charge transport across the organic thin film layers plays a key role. Concerning the OLED devices, the charge injection process requires promotion of an electron or hole from the metal junctions into one of the charge transport states (HOMO for hole transport and LUMO for electron transport) of the organic thin film layers. It is desirable that the injected holes and electrons have both large and similar mobility, in order to recombine close to the electro luminescent layer and to prevent luminescence quenching close to the electrode's interface [55][56]. On the other hand, in OPVs, the charges created upon photoexcitation need to be efficiently transported and collected at the electrode's Contacts, and stored under 52.

The form of electrical energy. In OPVs the optical band gap limits the portion of the solar spectrum that is absorbed by the organic cell [57][58].

HOMO, LUMO gap energies can be experimentally measured by spectroscopic and conductivity methods. For instance, they can be derived from absorption and reflectance spectra, from electrical conductivity measurements and from photoconductivity techniques[59][60].

1-5: Magnetic Sensitivity :

The magnetic behavior of the materials varies depending on the number of individual electrons in the outer orbitals as well as on the distance between the atoms and the radius of the atom.

The magnetic spin moments contribution of the electron and the orbital moments of the magnetic moments express as the following equation [61]:

$$\mu_{S+L} = g [S (S+1)] + [1/4L (L+1)] 1/2 \dots \dots \dots (1)$$

Where:

μ = Total magnetic moments

g = gyromagnetic ratio

S = Total spin angular moment

L = Total orbital angular moment

The electronic structure determination that needs to take the round moment into consideration, it was found that when studying the transition metals complexes of the first-series have a very low angular orbital momentum contribution so this magnetic momentum is measuring only by spin angular moment relationship [61].

$$\mu_S = g [S (S+1)] 1/2 \dots \dots \dots (2)$$

The angular orbital moment for transition metals and lanthanides is significant take into consideration.

Interest in the number of individual electrons is particularly important when studying the complexes of transitional metals . The μ values are change significantly with the change in the number of individual 5d electrons, the resulting error of taking the spin moment just a little consideration.

Then equation of the spin moment become

$$\mu_S = g [S (S+1)] 1/2 = [4S (S+1)] 1/2 \dots \dots \dots (3)$$

Where

$g = 2.00023$ Bohr magnetons = 2

Since the

$S=1/2, 1, 3/2$, for non-duplex electrons, the equation is written as follows

$$\mu_S = [n (n+2)] 1/2 \dots \dots \dots (4)$$

Where (n) is the number of non-duplex electrons and this equation is often used. [61]

Conclusion :

Thiadiazole showed interesting optical, electronic, and chemical properties. Thiadiazole exhibit diverse biological activities, possibly due the present of -N=C-S moiety. Thiadiazole are very interesting compounds due to their important applications in many pharmaceutical biological and analytical fields.

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