Important of Azoles

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Received: December 9, 2018  Accepted: December 22, 2018  Online Published: January 5, 2019

Abstract
Azoles are one of a cyclic derivatives of chemical heterocyclic chemical and organic compounds including a five member di unsaturated ring structure composed of two nitrogen atoms at position (3 and 4) and one sulfur atom at position (1).

Most of prepared work on the four thiadiazoles has been on the 1, 3, 4-thiadiazoles. Physical, theoretical, and spectroscopic properties have been reviewed.

Keywords: Azoles, Thiadiazole, Amino.

1. Introduction
The 1,3,4-thiadiazole, they could determine the structure of the molecule (5), fig(1).

![Fig. (1) Bond lengths (Å) and angles in 1,3,4-thiadiazole](image)

According to methods of spectroscopy, the π-electron delocalization decrease in the order: 1,2,5-thiadiazole > thiophene > 1,3,4-thiadiazole > 1,2,5-oxadiazole.

Zahradnik and Koutecky(6) made a series of studies and found that the calculated bond orders show a larger π-electron delocalization in the 1,2,5 than in the 1,3,4 isomer, in agreement with the results of Bak.
The formal double bonds have a lower bond order in the 1,2,5 than in the 1,3,4-isomer, whereas the reverse is true for the formal single bonds.

![Fig. (2) π-Electron distribution and bond orders in 1,3,4-thiadiazole](image)

U.V spectral features have been investigated, the parent molecule absorbs at 229nm, and substituents with lone pairs cause bathochromic shifts\(^7\).

The aromatic thiaadiazole nucleus is associated with a variety of pharmacological actions, such as fungicidal\(^8,9\), controlling blood pressure\(^10\) and can affect central nervous system\(^11\). These activities are probably due to the presence of the -N=C-S- moiety. Furthermore, a great number of variously substituted 1,3,4-thiadiazoles have been synthesized and tested for their different activities\(^12-18\).

**2-Amino-5-mercapto-1, 3, 4-thiadiazole**

2-Amino-5-mercapto-1,3,4-thiadiazole is capable of existing in four tautomeric form\(^19\):

![Fig.(3) The four tautomeric forms of 2-amino-5-mercapto-1,3,4-thiadiazole](image)
AMT stands for 2-amino-5-mercapto-1,3,4-thiadiazole, which also found under the chemical names of 5-amino-1,3,4-thiadiazole-2-thiol, 1,3,4-thiadiazole-2(3H)-thion-5-amino, 2-amino-1,3,4-thiadiazole-5-thiol and 2-mercapto-5-amino-1,3,4-thiadiazole. It should be noted that all have the same general formula C$_2$H$_3$N$_3$S$_2$.  

AMT is a white-yellowish powdered crystalline solid, with a molecular weight of 133.19g/mol, melt at 227°C.

3. Synthesis of 1, 3, 4-thiadiazole derivatives

Since thiadiazoles have a variety of potential biological activities and utilities as technologically useful materials, a number of methods for the preparation have been developed. Many synthesis of 1,3,4-thiadiazoles proceed from thiosemicarbazide or substituted thiosemicarbazide, for example thiosemicarbazide itself was shown to cyclize directly to 2-amino-5-methyl-1,3,4-thiadiazole [1] through the reaction with acetyl chloride:

\[
\text{H}_2\text{NNH}_2\text{C} \rightarrow \text{CH}_3\text{COCl} \rightarrow \text{C} \rightarrow \text{NH}_2
\]

This simple route to 2-amino-5-substituted-1,3,4-thiadiazoles seems to be quite general. A useful preparative method for 2-amino-5-mercaptop-1,3,4-thiadiazoles was developed by Guha which showed that when thiosemicarbazide is treated with carbon disulfide and potassium hydroxide, the potassium salt of thiosemicarbazide-4-dithiocarboxylic acid [2] was formed. Heating [2] to 140°C causes cyclization to the salt of 2-amino-5-mercaptop-1,3,4-thiadiazole [3]:

\[
\text{H}_2\text{NNH}_2\text{C} \rightarrow \text{CH}_3\text{COCl} \rightarrow \text{C} \rightarrow \text{NH}_2
\]
Hiremarth \(^{(24)}\) synthesized a series of 2-amino-5-[4’-(substituted)anilino]-methyl-1,3,4-thiadiazole \(^{(5)}\) through cyclocondensation of thiosemicarbazide derivatives \(^{(4)}\) with phosphoric acid.

\[
\begin{align*}
\text{R} & = \text{CH}_3, \text{OCH}_3, \text{Cl}, \text{Br} \\
\end{align*}
\]

Other papers\(^{(25-35)}\) prepared 3-aryl-1,2,4-triazolo[3,4-b][1,3,4] thiadiazole -6(5H)-thiones \(^{(7)}\) by the reaction of 3-aryl-4-amino-5-mercapto-1,2,4-triazoles \(^{(6)}\) with CS\(_2\) in the presence of pyridine.

\[
\begin{align*}
\text{Ar} & = p-\text{ClC}_6\text{H}_4, p-\text{NO}_2\text{C}_6\text{H}_4, p-\text{PhC}_6\text{H}_4 \\
\end{align*}
\]

**4. Thiadiazoles uses**

Among azoles, thiadiazole and its derivatives continue to draw the attention of synthetic organic chemists due to large group of compounds possessing a wide spectrum of uses.

Heterocyclic compounds possessing 1,3,4-thiadiazole ring system show antifungal, bacteriostatic as well as anthelmintic effects\(^{(34,35)}\). Compounds containing the above ring also exhibit anti-inflammatory, antimicrobial properties\(^{(36)}\) and the depression effect on the central nervous system\(^{(37)}\).

In the field of archaeological conservation, amino-mercapto-1,3,4-thiadiazole is the most widely used corrosion inhibitor in the treatment of bronze artifacts\(^{(38)}\).

The aim of applying corrosion inhibiting compounds are to prevent the conversion of nantokite (copper(I) chloride, CuCl) into paratacamite (basic copper(II) chloride, CuCl\(_2\).3(OH)\(_2\)) which causes major damage in archaeological copper artifacts\(^{(39)}\).
Furthermore, heterocycles have been put to much use in the chemistry of disperse dyes, for example, a series of monoazo disperse dyes [24] based on 2-amino-5-mercapto-1,3,4-thiadiazole was prepared by coupling with various N-arylmaleimides [40]:

![Chemical structure diagram]

These dyes have been found to give a wide range of color shades [41] with very good depth and levelness on fabric [42]. The yield fabrics showed moderate to good light fastness [43], very good to excellent washing [44], rubbing [45], perspiration [46], fixation [47], and sublimation fastness properties [48].

Therefore, thiadiazoles represent an important heterocyclic scaffold of compounds which display a wide range of different activities [49].
References

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