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Baghdad Science Journal **Vol.13(4)2016**

DOI: http://dx.doi.org/10.21123/bsj.2016.13.3.0762

Synthesis and Characterization of some New 1,3,4-Oxadiazole derivatives based on 4-amino benzoic acid

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Received 9/ 7/2015
Accepted 11 /5 /2015

Abstract:

Various of 2,5- disubstituted 1,3,4-oxadiazole (Schiff base, β- lactam and azo) were synthesized from 2,5-di (4,4′-amino-1,3,4-oxadiazole which usequently synth-esized from mixture of 4- amino benzoic acid and hydrazine arch of polyphosphorus acid. The synthesized compounds were cherecterized by using some spectral data (UV, FT-IR , and ^{1}H-NMR)

Key words: Oxadiazole, Schiff base, β- Lactam.

Introduction:

Oxadiazole is an important hetrocyclic ring presented in variety of boilogically active molecules inclusive of fungicideal, bactericidal, anticancer, antitubercular activities, etc[1].1,3,4-Oxa-diazole is the most thermally stable isomer which has attracted special ate-ntion, this is primarily due to the large number of uses in many diverse areas, including drugs, scintillation materials, dyes [2] and surface active agents [3].

It has been reported[4] that heterocyclic such as oxadiazoles are themselves important chemotherapyeutic agents and exhibit antitubercular, bacteriostatic, hypoglycemic, antiviral, antifungal, antithyroid, carcinostatic and strong herbicidal activities when properly substituted in 2-and 5- positions. Various 2,5-diaryl-2,5-dialky l-,and 2-alky l-5- aryl-1,3,4- oxadiazoles show herbicidal effect, especially against broad leafed weeds and grasses in crops such as rice and corn [5].

Material and Methods:

1-Synthesis of Bis(2,5-(4,4-diaminophenyl)- 1,3,4-oxaiazole [1]

A mixture of 4-amino benzoic acid (2.74g, 0.02mol), hydrazine hydrate (0.01) and (5ml) polyphosphorus acid was refluxed gently at (100-125) C^{o} with stirring for (4hr) until the solution turned dark brown. The reaction mixture was cooled then neutralized with sodium bicarbonate (10%) and the resulting solid was filtered off, dried and re-crystallized from absolute ethanol to give the desired oxadiazol deriveative

[6].The physical properties of compound [1] in Table (1).

2-General prparation of Schiff bases [2-4]

A mixture of compound[1] (0.-278g,0.001 mol) and appropriate aldehyde (0.002 mol) in absolute ethanol (15 ml) with the presence of (4-5) drops of glycial acetic acid was refluxed for (4hr). The solid was filtered off, dried[7] and recrystallized from appropriate solvent. The physical properties of compounds[2-4]in Table (1).

3-General preparation of β-Lactam compouneds [5-7]

A mixture of appropriate Schiff base (1 mol), chloro acetic acid (2 mol) and (2) drops of pyridine in dimethyl formamide (15ml) was refluxed after that adding of Triethyl amine (2ml) for (1hr).Evaporation of the solvents ,ice was added ,the solid formed was filtered and re-crystallized from appropriate solvent[8].The physical properties of compounds [5-7] in Table (1).

4-Synthesis of diazonium salt [8]

The diazonium salt [8] was prepared by using compound [1] (1g), $NaNO_2$ (0.5g), HCl (4ml), water (5ml) of low heat (0-5)C^0 [9]. The physical properties of compound[8] in Table(1).

5-Synthesis of compound [9]

Compound [8] (0.001mol) in absolute ethanol (20 ml) was admixed with ethyl aceto acetate (0.001mol) then refluxed for (7hr). The solid formed was filtered off, dried and recrystallized from absolute ethanol[10]. The physical properties of compound [9] in Table (1)

6-Synthesis of compound [10]

A mixture of compound[9] (0.01mol) and hydrazine hydrate (0.01mol) in absolute ethanol (25ml) was refluxed for (10hr).After evaporation of solution, the solid formed was filtered and re-crystallized from absolute ethanol. The physical properties of compound(10) compound in Table (1).

Results and Discussion

The synthesized of compounds [1-10] were shown in Scheme (1) and Scheme (3).The structure of the synthesized compound [1] has been characterized and confirmed by FT-IR spectrum besides Uv/Vis spectrum. The FT-IR spectrum of compound [1], Figure.(1),shows the appearance absorption band in the range (3460-3363) cm^{-1} which could be attributed to asymmetric and symmetric stretching vibration of the (NH_2),the (-C=N) stretching band at (1624) cm^{-1} of the oxadiazole ring .

The Uv/Vis spectrum of compound [1] Fig (8) showed the absrption bands at (227nm) (208nm), due to ($n\rightarrow\pi^*$) and ($\pi\rightarrow\pi^*$) transition.

The characteristic data reported in Table (3-1).

Compounds [2-4], the title compounds were synthesized from the re-action between compound [1] and several aldehydes in absolute ethanol and glacial acetic acid.

The structure of the synthesized compounds [2-4] has been characterized and confirmed by FT-IR spectrum besides the ^{1}H.NMR Analysis.

The FT-IR spectrum of compound (2) in Figure (2) shows the disappearance absorption band at (3460-3363) cm^- due to the asymmetric and symmetric stretching vibration of the (NH_2) group and appearance the (C=N) band of the imine in (1593) cm^- [1][11],also bands appear at (3066) cm^{-1}, (2981)cm^{-1} due to υ(C-H) aromatic, υ (C-H) aliphatic respectively, these bands and others are shown in Table (2).The ^{1}H.NMR spectrum of compounds [2],[3] and [4], Figure (10),Figure (11), Fig(12) respectively shows the following Characteristic chemical shifts (DMSO-d_6,ppm).The four aromatic protons appearat:(δ 7.283-8.979),(δ 6.532-7.976)

and(δ 7.226-8.501) due to aromatic protons.

The signal at (δ10.342, 9.867 and 9.664) attributed to (C-H) proton respectively.

Also the Methyl group resonate appear at(δ3.024), and the Methoxy protons appear at (δ3.644-4.018). Furthermore, the small peakat (δ 2.5) was due to DMSO.

The Uv/Vis spectrum of compound [4] Figure (9) showed the absorption bands at (243nm) (208nm), due to ($n\rightarrow\pi^*$) and ($\pi\rightarrow\pi^*$) transition.

Compounds [5-7], the title compounds were synthesized from the react-ion between Schiff bases [2], [6], [7] with chloro acetyl chloride in the presence of dimethyl formamide as a solvent.

The structure of the synthesized compounds [5-7] has been characterized and confirmed by FT-IR spectrum

The FT-IR Spectrum of com-pound [7] in Figure (10) shows the dis-appearance absorption band (C=N) of the imine in (1550)cm^{-1} and appearance of the (C=O) absorption band at (1701) cm^{-1}, (C-Cl) absorption band at (773) cm^{-1} ,Other bands were also abs-orbed in FT-IR spectra of these compounds which are listed in Table (2).

Compound [8] has been synthesized by the reaction between aromatic primary amine [compound 1] and nitrous acid obtained from sodium nitrite and hydrochloric acid .

The structure of the synthesized compound [8] has been characterized and confirmed by FT-IR spectrum. The FT-IR spectrum of compound [8] shows the disappearance absorption band at (3460-3363)cm^{-1} due to the asymmetric and symmetric stretching vibration of the (NH_2) group and appearance the $(N\equiv N)^+$ band of the diazonium group at (2476) cm^{-1} .Other bands were also absorbed in FT-IR spectra of this com-pound which are listed in Table (2).

Compound[9], the reaction of Diazonium salt with ethyl aceto acetate gives the compound [9] in the presence of absolute ethanol as a solvent.

The structure of the synthesized compound [9] has been characterized and confirmed by FT-IR spectrum. The FT-IR spectrum shows the disappearance absorption band at (2476)cm^{-1} due to the $(N\equiv N)^+$ group and appearance the (O-C=O) band of the carbonyl ester group at (1707)cm^{-1},also band appear at (1608)cm^{-1} due to the (C=O) carbonyl and band appear at (1508) cm^{-1} due to the (N=N).Other bands were also absorbed in FT-IR spectra of this compound which are listed in Table (2).

Compound [10] was synthesized from the reaction between com-pound [9] and hydrazine anhydrate (99%).

The structure of the synthesized compound [10] has been characterized confirmed by FT-IR spectrum. The FT-IR spectrum of compound [9] in Figure (6)shows the disappearance absorption band at(1707)cm^{-1}due to the (O-C=O) of the carbonyl ester group, and appearance of the (NH) band at (3140)cm^{-1}, and (C=O) of carbonyl group at (1681)cm^{-1},and appearance new group of (C=N) at (1600)cm^{-1}.Other bands were also absorbed in FT-IR spectrum of this compound which are listed in Table (2).

Table (1) Physical Properties and Structures of Compounds

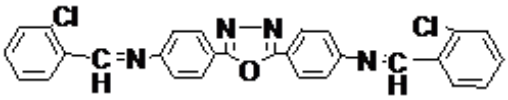
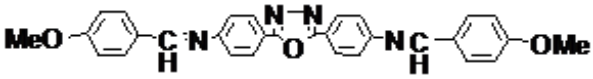
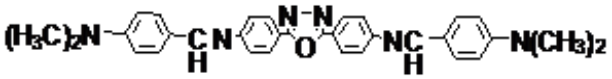
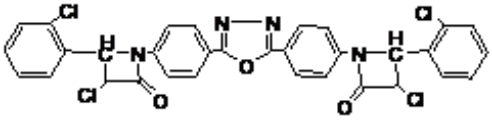
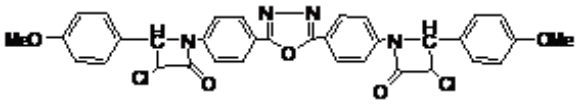
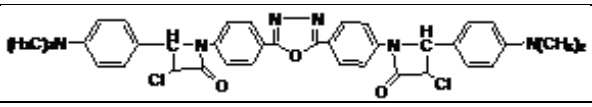
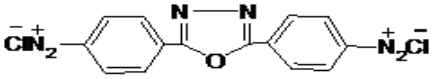
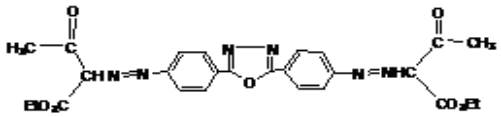
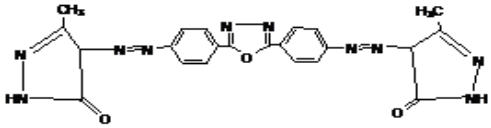
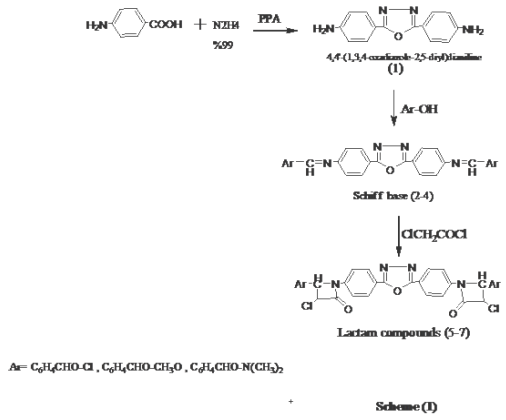
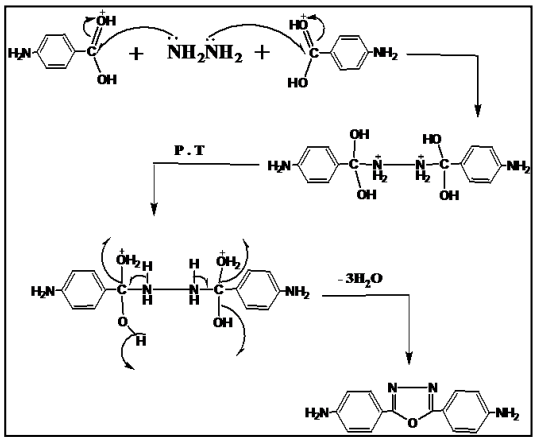
Co. no.	Structures	M.p. C0	Yield %	Color	Recry. solvent
1		256-258	90	Pale wight	Ethanol absolute
2		158-160	73	Yellow	Ethanol absolute
3		168-170	66	Pale orange	Ethanol absolute
4		218-220	35	Bile Green	Ethanol absolute
5		oily	68	wight	Benzene
6		138-140	40	Orange	Benzene
7		Oily	86	Black	Benzene
8		150-152	74	Orange	Ethanol absolute
9		152-154	44	Deep Orange	Ethanol absolute
10		123-125	86	Deep Orange	Ethanol absolute

Table (2): FT-IR spectral data of compounds

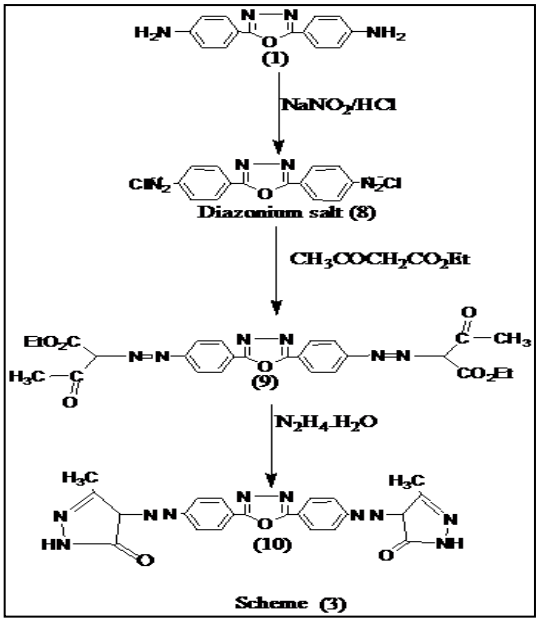
Co. No.	Name of compound	(C-H) υ cm^{-1} Aromatic	(C-H) υ cm^{-1} Aliphatic	υ(C=N) cm^{-1} cyclic	υ(C-O-C) cm^{-1}	Other band cm^{-1}
1	**4,4'-(1,3,4-oxadiazole-2,5-diyl)dianiline**	3232		1624	1172	NH_2 3460-3363
2	**4,4'-(1,3,4-oxadiazole-2,5-diyl)bis(N-(2-chlorobenzylidene)aniline**	3066	2981 2893	1624 Cyclic 1593 imin	1288	C-Cl 775
3	**4,4'-(1,3,4-oxadiazole 2,5-diyl)bis(N-(4-methoxybenzylidene)aniline**	3005	2981 2939	1627 Cyclic 1593 imin	1253	O-Me 1292
4	**4,4'-(4,4'-(1,3,4-oxadiazole 2,5-diyl)bis(4,1-phenylene)bis(azan-1-yl-1-ylidene)bis(methan-1-yl-1-ylidene)bis(N,N-dimethylaniline)**	3074	2854 2808	1581 Cyclic 1550	1161	C-N 1550
5	**1,1'-(4,4'-(1,3,4-oxadiazole-2,5-diyl)bis(4,1-phenylene)bis(3-chloro-4-(2-chlorophenyl)azetidin-2-one)**	345 338	2995	1635		C-Cl (phenyl) 783 C-Cl 768 C=O 1701
6	**1,1'-(4,4'-(1,3,4-oxadiazole-2,5-diyl)bis(4,1-phenylene)bis(3-chloro-4-(4-methoxyphenyl)azetidin-2-one)**	3050 3043	2976 2941	1600		(C-OMe) 1315 C-Cl 771 C=O 1708
7	**1,1'-(4,4'-(1,3,4-oxadiazole-2,5-diyl)bis(4,1-phenylene)bis(3-chloro-4-(4-dimethylamino)phenyl)azetidin-2-one)**	3061	2999	1653		($C-NMe_2$) 1369 C-Cl 773 C=O 1701
8	**Diazonium Salt**	3047		1608	1246	N≡N 2476
9	**Diethyl 2,2'-(4,4'-(1,3,4-ooxadiazole-2,5-diyl)bis(4,1-phenylene))bis(diazene-2,1-diyl)bis(3-oxobutanoate)**		2993 2906	1575		C=O Ester 1707 C=O 1608 N=N 1508
10	**4,4'-(4,4'-(1,3,4-oxadiazole-2,5-diyl))bis(4,1-phenylene))bis(diazene-2,1-diyl)bis(3-methyl-1H-pyrazol-5(4H)-one)**		2981 2893	1577	1242	C=O 1681 New C=N 1600



The suggested mechanism for compound [1] is shown in scheme(2).



Scheme(2)



Scheme (3)

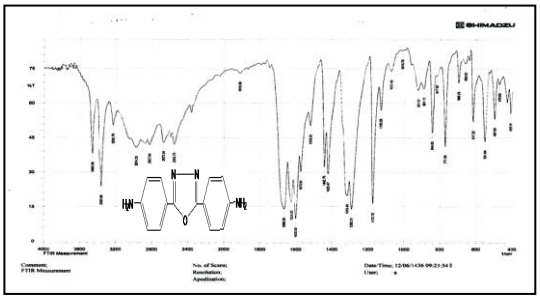


Fig.(1) FT-IR of compound[1]

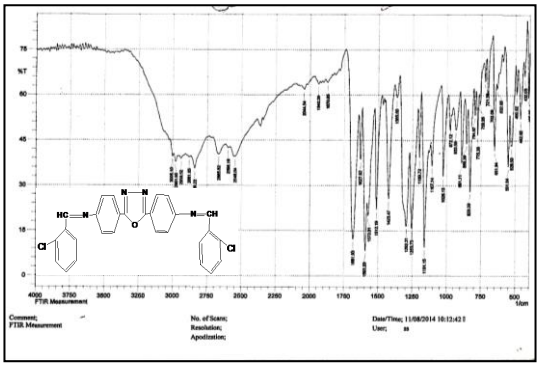


Fig. (2) FT-IR of compound[2]

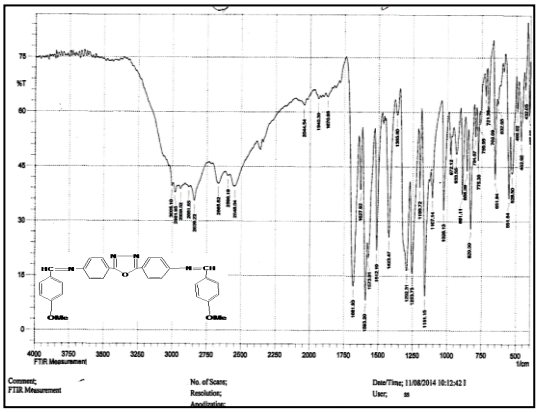


Fig.(3) FT-IR of compound[3]

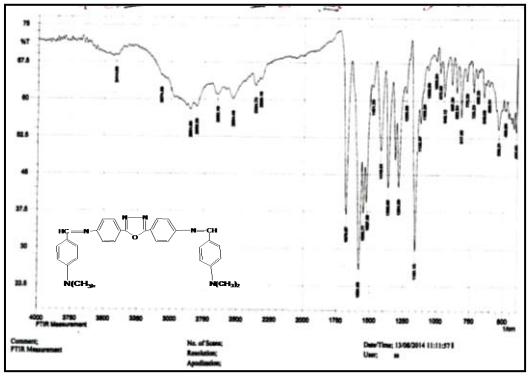


Fig.(4) FT-IR of compound[4]

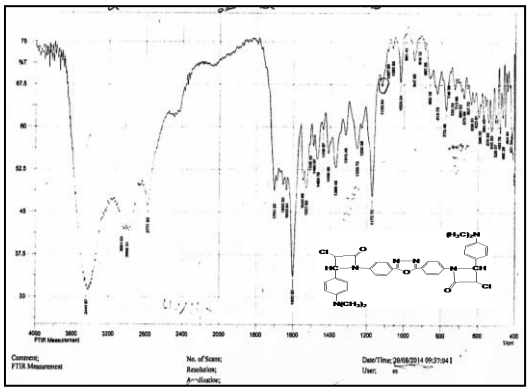


Fig.(5) FT-IR of compound[7]

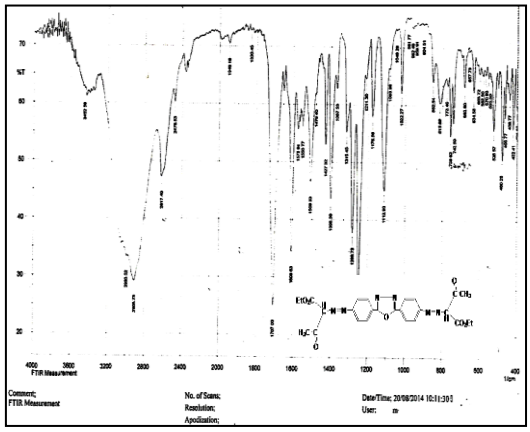


Fig. (6) FT-IR of compound [9]

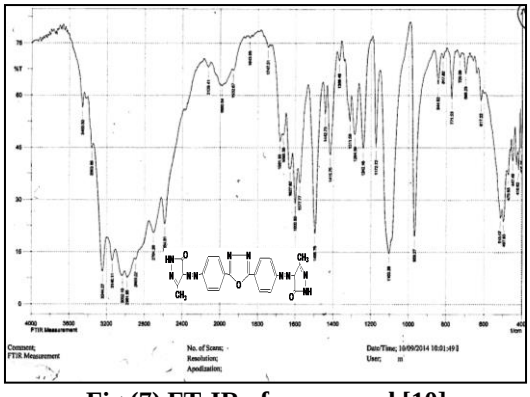


Fig.(7) FT-IR of compound [10]

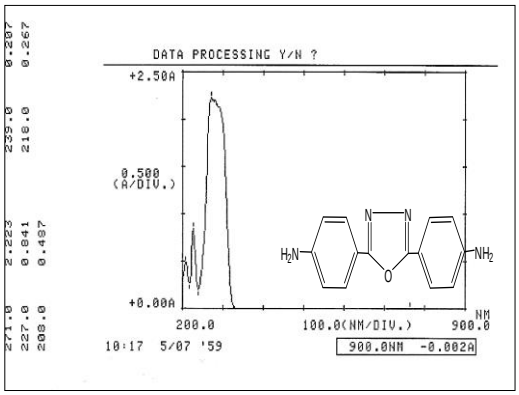


Fig.(8) U.V. Spectrum of compound [1]

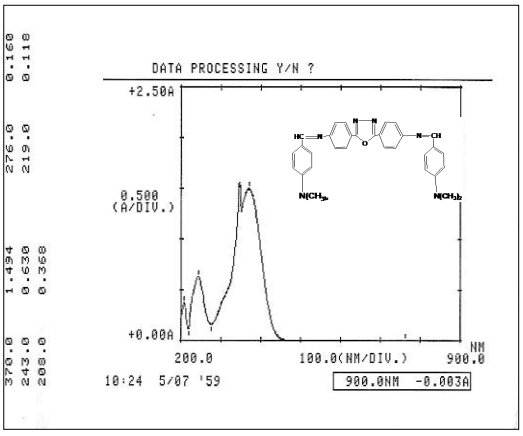


Fig.(9) U.V. Spectrum of compound [4]

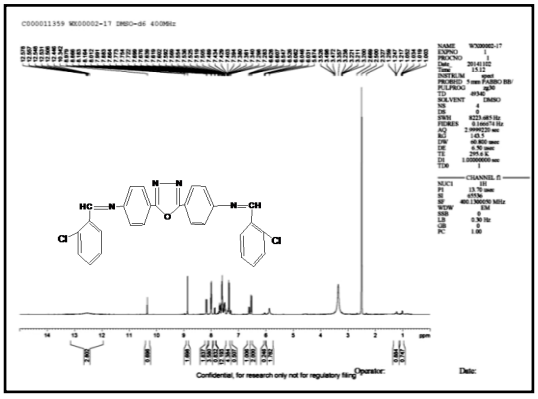


Fig.(10) HNMR of compound [2]

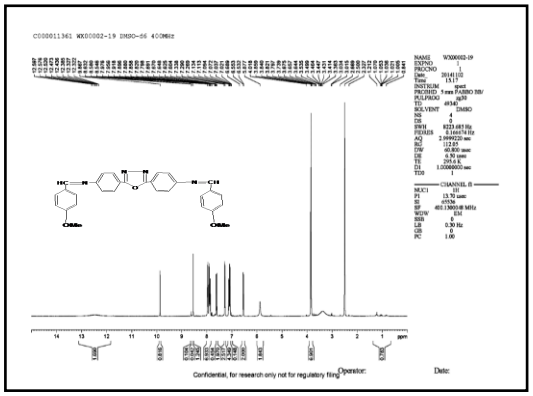


Fig.(11) HNMR of compound [3]

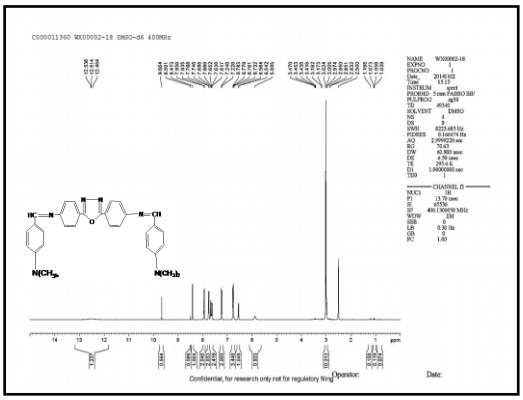


Fig.(12) HNMR of compound [4]

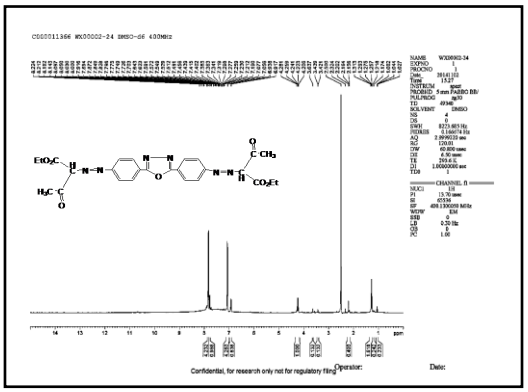


Fig.(13) HNMR of compound [9]

References:

[1] Joule, J. A.; Mills, K.; and Smith, G. F.2011. Heterocyclic compound. H C;3: 452.

[2] Rakesh, R. S; Prabhakar, Y. S. 2009. Oxadiazole: A biologically important heterocycle. DC; (1):130-140.

[3] Peng. F.; Zhi, Z.; Xin, P. H.; Zi, Y. Z.; and Rong, L. Z. 2004. Synthesis of Triazoles, Oxadiazoles and Condensed Heterocyclic Compounds Containing Cinchopheny and Studies on Biological Activity of Representative Compounds. JCC S; 51(2): 315-319

[4] Katritzky, A. R.; Tymoshenko, D. O.; Monteux, D.; Vredensky, V. and Nikonove, G. 2000. A new three-carbon synthon for efficient synthesis of benzannelated and 1-(2-arylethenyl) heterocycles JOC; 65 (23):8059-62.

[5] Manish, K. M.; Gupta, A. K.; Negi S.; Meenakshi, B. 2010. Synthesis

of some new oxadiazole with antimicr-obial activity. IJPSR. 1(3):172-177

[6] Naser, F. and Sattar, E. 2013. One-pot synthesis of 1,3-thiazolidin-4-one using Bi $(SCH_2COOH)_3$ as catalyst .C CL; 24 : 389–391.

[7] Fatehia, K. M. 2010. Synthesis, reactions and antimicrobial activity on some novel phthalazinones derivatives. PRLDCS;1 (1): 20-31

[8] Lud, S. Q.; Steenackers, M.; Bruno, P.; Gruen, D. M.; Feulner, P.; Garrido, J. A. and Stutzmann, M. 2006. Chemical Grafting of Biphenyl Self-Assembled Monolayers on Ultrananocrystalline Diamond.JACS;128(51): 16884–91.

[9] Zaranappa; Hosadu, M. V.; Mayasandra, R. L. and Basavanneppa, C. G. 2012. Synthesis and Antioxidant Activity of 3- Substituted Schiff bases of Quinazoline-2,4-diones,IJCT R;4(4):1527-1533.

[10] Ameta, K. L.; Nitu, S. R. and Biresh, K. 2011. Synthesis of Some Novel Chalcones and their facile One-Pot conversation to 2-Amino benzene-1,3-dicarbonitrile using Malononitrile. AUBC;20 (1):15 -24.

[11] Mousumi, C.; Sanjay, B.; Sunita, B. and Tejpal, S. C. 2012. Microwave Assisted Synthesis of Schiff Bases: A Green Approach. IJCRE. 10(1):53-57.

تحضير وتشخيص اوكسادايازول-5,2 4,3,1 اوكسادايازول مبنيا على-4 امينو حامض البنزويك

شذى فاضل الزبيدي **بشرى كريم حمد** **بان ذنون اسماعيل**

قسم الكيمياء، كلية العلوم للبنات، جامعة بغداد.

الخلاصة :

تم تحضير -5,2 ثنائي معوضات -4,3,1 اوكسادايازول مختلفه (قواعد شيف ,بيتالاكتام, وازو) من الماده الاساسيه -5,2 ثنائي -4′,4 ثنائي امينو -4,3,1 اوكسادايازول التي تم تحضيرها من حامض -4 امينو البنزويك وهيدرازين بوجود حامض الفوسفور المتعدد.

تم تشخيص المركبات المحضره باستخدام بعض الطرق الطيفيه ,Uv , FT-IR, ^{1}H-NMR

الكلمات المفتاحية: اوكساديازول، قاعدة شف، بيتا لاكتام.