Open Access
Baghdad Science Journal **Vol. 13(2s(Supplement))2016**
The 2nd National Conference of Chemistry

DOI: http://dx.doi.org/10.21123/bsj.2016.13.2.2NCC.0289

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

Shatha F. Al-Zobaydi ***Bushra Karim***
Sanaa A. Al-Sahib ***Ban Dha. Ismael***

Department of Chemistry, College of Science for Women, University of Baghdad

E-mail: sanaa_abdul@yahoo.com

Received 5/10/2015
Accepted 20/12/2015

Abstract:

In this research various of 2,5-disubstituted 1,3,4-oxadiazole (Schiff base, oxo-thiazolidine , and other compounds) were synthesized from 2,5-di(4,4′- amino-1,3,4-oxadiazole) which use quently synthesized from mixture of 4-amino benzoic acid and hydrazine in the presence of polyphosphorus acid. The synthesized compounds were characterized by using some Spectral data (UV, FT-IR, and $_1$H-NMR).

Key words: Oxadiazole, Schiff based, thiazolidine.

Introduction:

Heterocyclic compounds are those cyclic compounds in which one or more of the ring carbons are replaced by another atom. Oxadiazole are aromatic rings with three hetero atoms, two nitrogen and one oxygen atoms, where N and O as donor atoms, and resemble to the triazole ring in that they belong to the same aromatic hetero-cyclic class. 1,3,4-Oxadiazole is the most thermally stabilized isomer which has attracted special attention, this is primarily due to the large number of uses in many diverse areas, including drugs, scintillation materials, dyes[1] and surface active agents [2].It has been reported [3]. Those hetero-cycles such as oxadiazoles are themselves important chemotherapeutic agents and exhibit antitubercular, bacteriostatic, hypo-glycemic, antiviral, antifungal, antithyroid, carcinostatic and strong herbicidal activities when properly substituted in 2- and 5- pos-itions. Variously 2, 5-diaryl-2, 5-dialkyl-and 2-alkyl-5-aryl-1,3, 4-oxadiazoles showed herbicidal effect especially against broad leafed weeds and grasses in crops such as rice and corn [4].

Materials and Methods:

The FT-IR spectra in the range (4000-200) cm-1 were recorded as KBR disc on a Shimadzu IR prestige -21 spectrophotometer ,UV-visible spectra in the range (200-1100) nm wererecorded on a using Shimadzu UV-vis .160A. UItra-violet spectrophotometer. Melting points were recorded on a hot stage Gallen Kamp melting point apparatus.

1H-NMR spectra were recorded 400 MHZ operating at 400 MHZ with tetra methylsi-lane as internal standard in CDCI3 and DMSO-d6 as solvent measurements were made at Mangdil chemical and pharm-aceutical center Wuhan City China. All chemicals used were analytical analar and of highest purity available from BDH, Fluka and Aldrich companies.

Synthesis of Bis (2,5-(4,4-diamino-phenyl)-1,3,4-oxadiazole (1):

A mixture of 4-amino benzoic acid (1.374g, 0.01mol), with 99% hydrazine (3.2g,0.01 ml) and polyphosohorus acid (5 ml). The mixture was refluxing at (120-125)C^0 with stirring for (4 hrs). The reaction mixture was cooled at room temperature and neutralized with a solution of 5% sodium bicarbonate. The obtained solid was filtered off. The products dried and re-crystallized using absolute ethanol to give the desired oxadiazole derivative [5] .The physical properties of compound (1) are listed in Table (1).

Synthesis of Compound (2):

Compound (1) (0.25g, 0.1 mol) in absolute ethanol (20 ml) was admixed with [(1.14g,0.2 mol) of KOH and (1.52,0.2 mol) of CS_2] then refluxed for (1hrs) in water bath, after evaporation of solution. (0.1g, 0.2mol) of hydrazine hydrate (80%) was added and refluxing for (4hrs). The mixture was acidified with (HCl 20%) the product formed was filtered off, dried and re-crystallized from absolute ethanol [6]. The physical properties of compound (2) are listed in Table (1).

Synthesis of Compound (3):

Compound (2) (0.4g,o,1 mol) in absolute ethanol (25 ml) was admixed with hyrazin hydrate (80%)(0.1g,0.2mol) then refluxed for (10hrs), after evaporation of solution . The solid formed was filtered off. Dried and re-crystallized from absolute ethanol [7].The physical properties of comp-ound (3) are listed in Table (1).

Synthesis of Compound (4):

A mixture of compound (1)(0.25g,0.1 mol),(0.002 mol)of P-chlorophenyl isothi-ocyanate in ethanol absolute (20 ml) was refluxed for (7hrs). The mixtures were cooled at the room temperature, filtrate and re-crystallized from ethanol [8].The physical properties of compound (4) in Table (1).

General Preparation of Schiff bases (5-7):

A mixture of compound (1) (0.278g, 0.1 mol) and appropriate aldehyde (0.2 mol) in absolute ethanol (15 ml) with the presence of (4-5) drops of glacial acetic acid was refluxed for (4hrs). The solid was filtered off, dried and re-crystallized from appro-priate solvent [9]. The physical properties of compounds (5-7) are listed in Table (1).

General Preparation of Thiazolidin of Compounds (8-10):

A solution of mercapto acetic acid (0.9g,0.1 mol) in dry benzene (15 ml) was added slowly to (0.1mol) of compounds (5,6,7) respectively in benzene (15 ml). The addition continued about (10 seconds) with stirring then the mixture was refluxed for (10 hrs). The excess of the solvent was evaporated and the residues were treated saturated solution of sodium bicarbonate, solid precipitate was re-crystallized from absolute ethanol and water (1:1)[10]. The physical properties of compounds (8-10) shown 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) in Figure (1) shows the appe-arance absorption band in the range (3460-3363) cm^{-1}which could be attributed to

asymmetric and symmetric stretching vibr-ation of the (NH_2),the (-C=N) stretching band at (1596) cm^{-1} of the oxadiazole ring. Other bands were also absorbed in FT-IR spectrum of this compound which are listed in Table (2).The Uv/Vis spectrum of compound (1) Figure (6) showed the absorption bands at (227nm) (208nm), due to ($n \rightarrow \pi^*$) and ($\pi \rightarrow \pi^*$) transition.

The structure of the synthesized compound (2) has been characterized and confirmed by FT-IR spectrum. The FT-IR spectrum of compound (2) in Figure (2) shows the (NH) band at (3213) cm^{-1}[11], the (C=S) band at (1176)cm^{-1} . Other bands were also absorbed in FT-IR spectrum of this compound are listed in Table (2).

Compound (3) was synthesized from the reaction between compound (2) and hydrazine anhydrate. The structure of the synthesized compound (3) has been charac-terized and confirmed by FT-IR spectrum besides Uv/vis spectrum. The FT-IR Spectrum of compound (3) in Figure (3) shows the appearance absorption band at (3417-3406)cm^{-1} due to the asymmetric and symmetric stretching vibration of the (NH_2) group and appearance the (NH) band at (3255)cm^{-1} and the (C=S) band at (1257cm^{-1} Other bands were also absorbed in FT-IR spectrum of this compound which are listed in Table (2).The Uv/Vis spectrum of compound (3) Figure (7) showed the absorption bands at (281nm) (258nm), due to($n \rightarrow \pi^*$) and ($\pi \rightarrow \pi^*$), and ($n \rightarrow \delta^*$) at (231 nm) transition.

The structure of the synthesized compound (4) has been characterized and confirmed by FT-IR spectrum .The FT-IR spectrum of compound (4) in Figure (4) shows the (NH) band at (3236)cm^{-1} ,the (C=S) band at (1176)cm^{-1} , and(C-Cl) band at (771)cm^{-1} .Other bands were also absorbed in FT-IR spectrum of this compound are listed in Table (2).

The compounds (5-7), were synthesized from the reaction between compound (1) and several aldehydes in absolute ethanol and glacial acetic acid. The structure of the synthesized compounds (5-7) has been characterized and confirmed using FT-IR spectra besides Uv/vis spectrum and the ^{1}H.MR spectra.

The^{1}H.NMR spectrum of compounds (5),(6) and (7) in Figure (9), Figure (10) and Figure (11) respectively showed chara-cteristic Signals at (δ 7.226-8.501) due to (m,8H aromatic-CH) respectively. Also signal at (δ 3.024) (S, 6H, CH_3) of compound (5), and at (δ 3.644-4.018) (S, 3H, C-OCH_3) of compound (6).

The signals at (δ 9.664, 9.867 and 10.342) (s, 1H, HC=N) [12].The Uv/Vis spectrum of compound (5) Fig (8) showed the absorption bands at (243nm) (208nm), due to ($n \rightarrow \pi^*$) and ($\pi \rightarrow \pi^*$) transition.

The structure of the synthesized compounds (8-10) have been characterized and confirmed by FT-IR spectrum besides the ^{1}H-NMR analysis for some of them. The FT-IR spectrum of compound (8) in Figure (5) shows the appearance of (C-S) band at (1095)cm^{-1}[13,14]and the carbonyl group band of the oxothiazolidine ring at (1735)cm^{-1} .Other bands are shown in Table (2).The ^{1}H-NMR spectrum of compound (10) in Figure (12) showed characteristic signals at (δ 2.5) was due to DMSO[15]The signal at δ3.023 (s,1H-S-CH) of thiazolidine ring, and also absorption δ 3.102 (s,1H,N-CH3) , and δ (6.661-7.814) (m,8H aromatic –CH).

Table (1) Physical Properties and Structure of Compounds

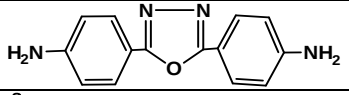
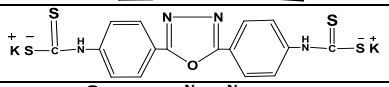
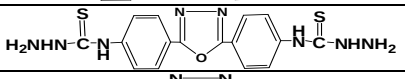
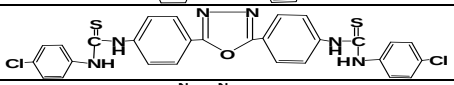
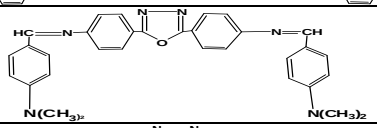
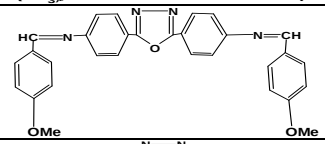
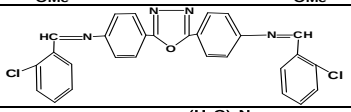
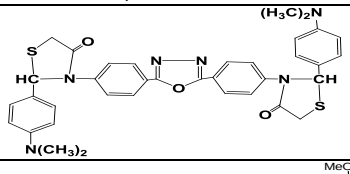
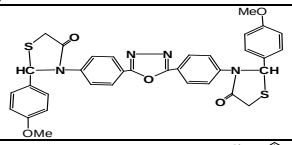
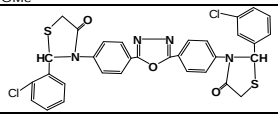
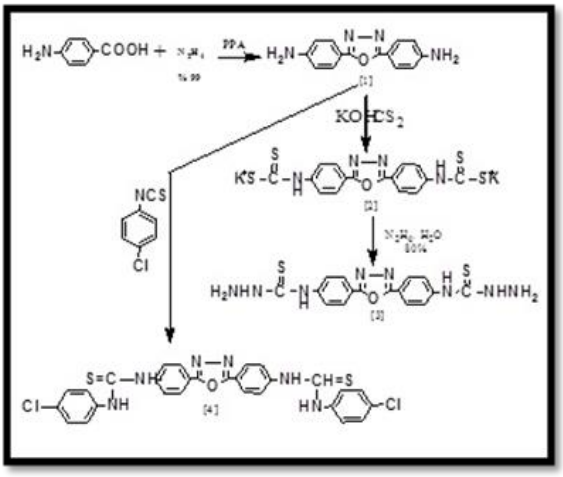
Comp. No	Structure	M.P.°C	Yield%	Color
1		187-189	90	White
2		Oily	78	Dark Brown
3		248-250	80	Pale White
4		190-192	68	White
5		218-220	35	Pale Green
6		168-170	66	Orange
7		158-160	73	Yellow
8		157-159	89	Dark Brown
9		Oily	85	Brown
10		248-250	66	White

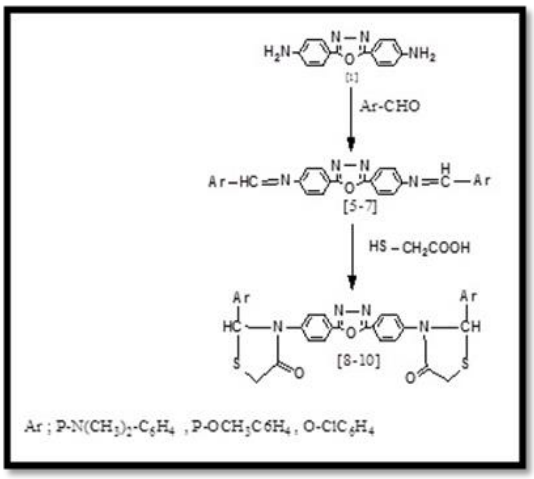
Table (2): FT-IR Spectral data of Compounds

Comp. No	Name of Compound	υ (C-H) cm^{-1} Aromatic	υ (C-H) 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	2997	3100	1596	1172	NH_2 3460-3363
2	Potassium 4,4'-(1,3,4-oxadiazole-2,5-diyl)bis (4,1-phenylene) dicarbamodithioate	2903		1583	1188	C=S 1176 N-H 3213
3	N,N'-(4,4'-(1,3,4-oxadiazole-2,5-diyl) bis(4,1-phenylene) bis(hydrazinecarbothioamide)	2938		1604	1172	C=S 1257 N-H 3255
4	1,1'-(4,4'-(1,3,4-oxadiazole-2,5-diyl)bis(4,1-phenylene) bis(3-(4-chlorophenyl) thiourea	2938		1681	1178	C-Cl 1037 C=S 1176
5	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)	2953	2854 2808	1581 Cyclic 1550 Imin	1161	C-N 1050
6	4,4'-(1,3,4-oxadiazole 2,5-diyl)bis(N-(4-methoxybenzylidene)aniline	2927	2981 2939	1627 Cyclic 1593 Imin	1253	O-Me 1292

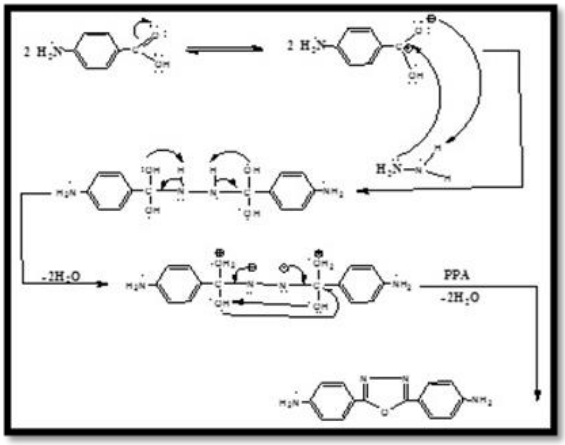
7	4,4'-(1,3,4-oxadiazole-2,5-diyl)bis(N-(2-chlorobenzylidene)aniline	2999	2981 2893	1624 Cyclic 1593 Imin	1288	C-Cl 775
8	3,3'-(4,4'-(1,3,4-oxadiazole-2,5-diyl)bis(4,1-phenylene)bis(2-(4-(dimethylamino)phenyl)thiazolidin-4-one)	2853	2916 2808	1560 Cyclic 1539 Imin	1168	C-N 1030 C-S 1095 C=O 177
9	3,3'-(4,4'-(1,3,4-oxadiazole-2,5-diyl)bis(4,1-phenylene)bis(2-(4-(methoxy)phenyl)thiazolidin-4-one)	2989 3090	2910 2815	1620 Cyclic 1590 Imin	1165	O-Me 1288 C-S 1090 C=O 1730
10	3,3'-(4,4'-(1,3,4-oxadiazole-2,5-diyl)bis(4,1-phenylene)bis(2-(2(chloro) phenyl)thiazolidin-4-one)	2960 3062	2924	1645 Cyclic 1585 Imin	1175	C-S 1099 C=O 1732



Scheme (1) Mechanism preparation of comp.(1-4)



Scheme (3) Mechanism preparation of compound (5-7) and compound (8-10)



Scheme (2) Mechanism preparation of compound (1)

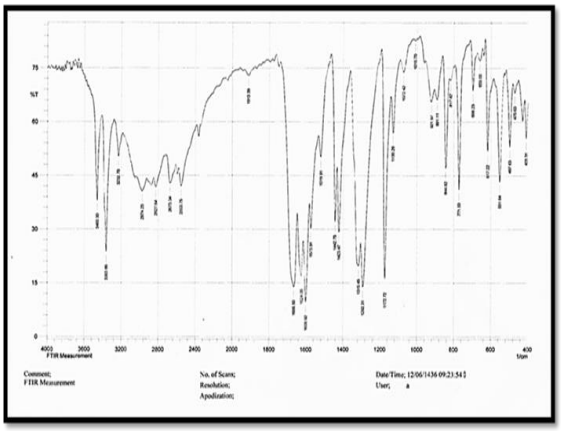


Fig. (1): FT-IR of compound (1)

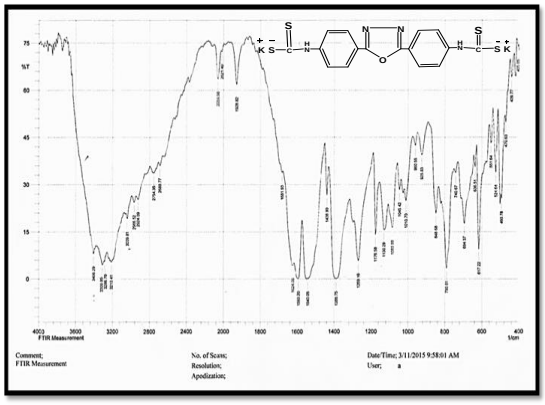


Fig. (2): FT-IR of compound (2)

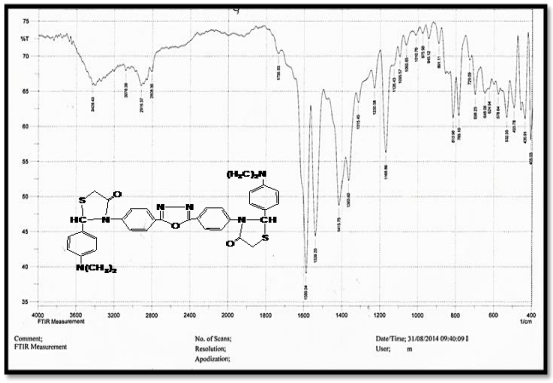


Fig. (5): FT-IR of compound (8)

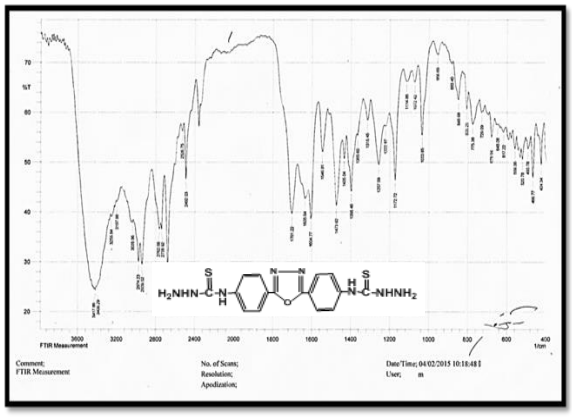


Fig. (3): FT-IR of compound (3)

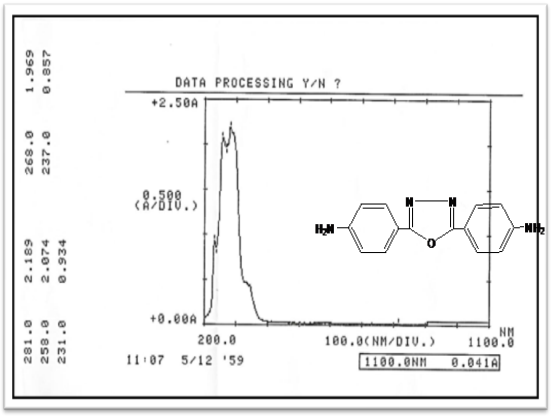


Fig. (6): U.V Spectrum of compound (1)

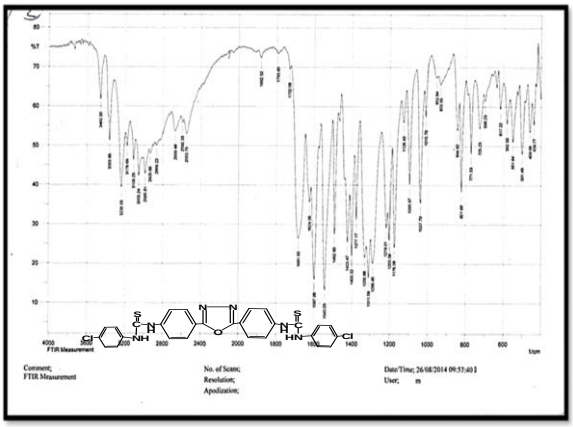


Fig. (4): FT-IR of compound (4)

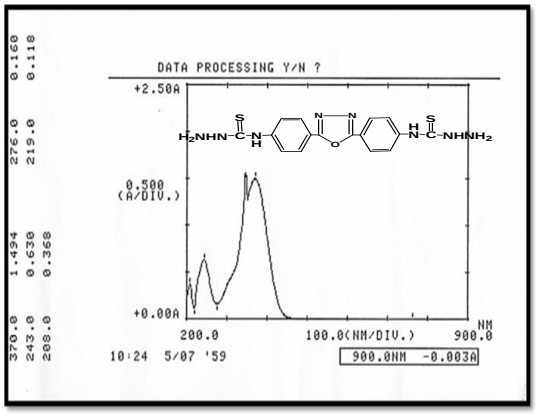


Fig. (7): U.V. Spectrum of compound (3)

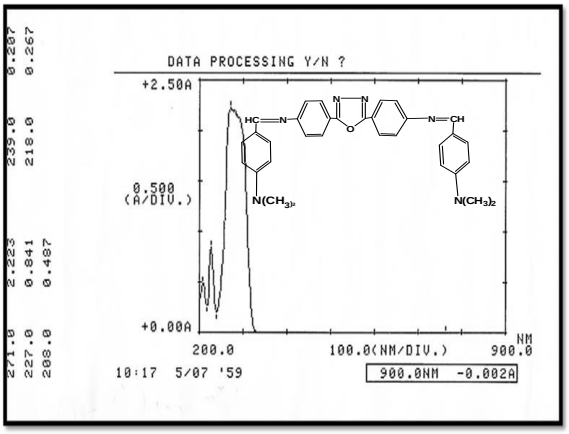


Fig. (8): U.V. Spectrum of compound (5)

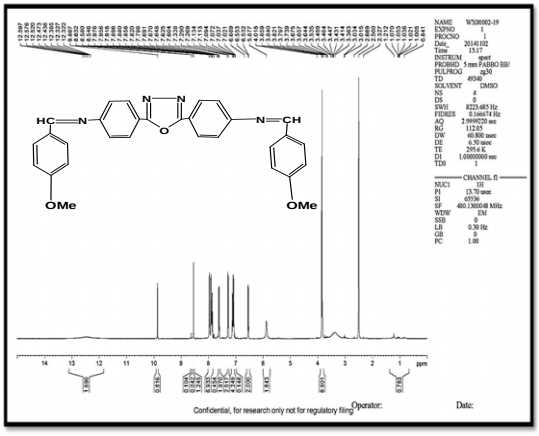


Fig. (10): HNMR of compound (6)

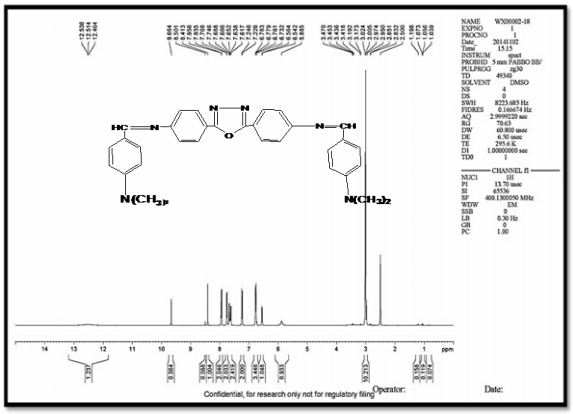


Fig. (9): HNMR of compound (5)

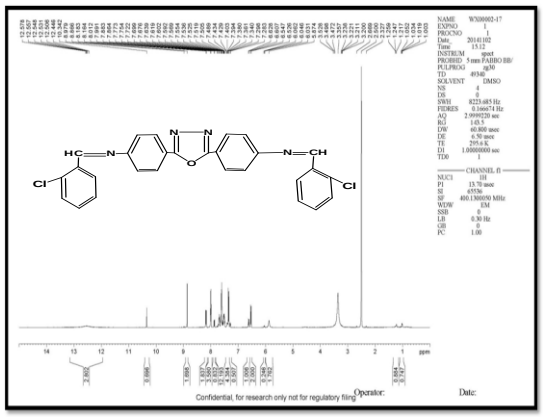


Fig. (11): HNMR of compound (7)

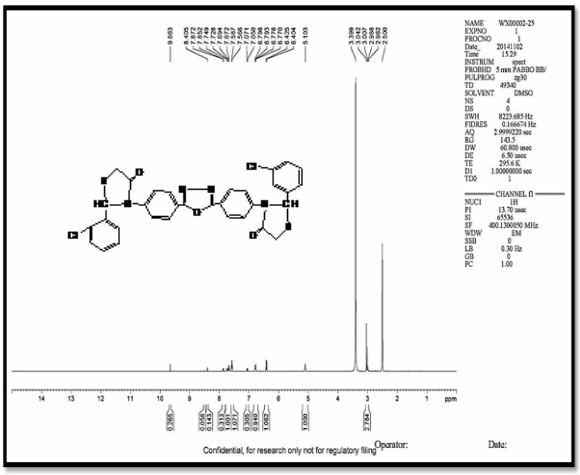


Fig. (12): HNMR of compound [10]

References:

[1] Bahl, A. and Bah, B. S. 2000. Advanced Organic Chemistry, New Delhi Sc. Chand Company limited, p-1201.

[2] Shivi, B. and Monika, G. 2011. Oxadiazole as antimicrobial agents: An overview. J. Chem. Pharm. Res., 3(3):137-1471, 3, 4-

[3] Ladva, K., Patel, P. and Parekh, H. 1966. J. Chem. ,35N:1062

[4] 4-Frump. J. A. 1971. Synthesis, characterization of some new heterocyclic compounds and evaluating their biological activity , Synthesis and characterization of 4-amino benzoic Chem. Rev., 71;483

[5] Attia, A. and Abdel-Salam, O. I. 1977. acid, Egypt. J. Chem ,40(5):363.

[6] Shunxue, Z. Anxiong, C. L.; Bin Q. and Hengshan,. D. 2003. Synthesis and, Molecu-les, 6(12): 92.

[7] Zaranappa, H.; Lokesh, M. and Gowdars-hivannanavar, B. 2012. Synthesis and Anti-oxidant Activity of 3-Substituted Schiff bases of Quinazoline-2,4-diones.Int J. Chem Tech Res.,4(4):1527-1533.

[8] Masury, A.. EL, Fahmy and Abdel Wahab, S. H. 2000. Synthesis and antibacterial activities of 2,4-thazolidinedione derivatives, Moleules, N5:1429-1438,

[9] Liang, W. and Chengyan, H. 2010. Synthesis of oaryloxime, Molecules. N11:532.

[10] Johnson, S. M.; Palanathan, S. K.; Mohamedmohaiden, N. N.; Purkey. H. E.; Nichols. C.; Chiang, K. P.; Walkup, T.; Sacchettini. J. C. and Sharp-less, K. B. Kelly. 2005. Synthesis and evaluation of a class of new coumarin triazolederivatives, J.W.J. Med.Chem.48:1576.

[11] Ameta, K. L.; Nitu, S. Rathore, and Biresh, K. 2011. Synthesis Of Some Novel Chalcones and their facile One-Pot conversation to 2-Amino benzene-1,3-dicarbonitrile using Malono nitrile. -ARS Docendi Publishing House,20 (1):15 -24.

[12] Ajaypalprajapati, A. and Chourasia, K. P. 2011. Amicrowave synthesis and characterization of some quinoline derivatives and tested their anti microbialactivity. International Journal of Pharmacy Research and Development (IJPRD). 2:53-57.

[13] Hoyar. S. 2005. Synthesis and charact-erization of some new Benzimidazole Derivatives, M.Sc. Thesis, Baghdad University.

[14] Silverstien. R. M. 1963. Spectrophotometric identificationof organic compounds. 3rd ed.:113-114.15-El-Masry.

[15] H.; Fahm. H. and Ali Abdelwahed. S. H. 2000. Synthesis and Antimicrobial Activity of Some New Benzimidazole Derivatives. Molcules. 5:1429-1438.

تحضير وتشخيص بعض المشتقات الجديدة من 1,3,4 اوكسادايازول مبنيا على 4 امينوحامض البنزويك

شذى فاضل الزبيدي **بشرى كريم حمد**
سناء عبد الصاحب عبد الكريم **بان ذنون اسماعيل**

قسم الكيمياء، كلية العلوم للبنات، جامعة بغداد

الخلاصة:

تم في هذا البحث تحضيرقواعد شف وثايوزولدين ومشتقات اخرى جديده لمركب2,5 ثنائي معوضات 1,3,4 اوكسادايازول مختلفة من الماده الاساسية 2,5 ثنائي 4,4` ثنائي امينو 1,3,4 اوكسادايازول التي تم تحضيرها من حامض 4 امينوحامض البنزويك وهدرازين بوجود حامض الفوسفور المتعدد . تم تشخيص المركبات باستخدام بعض الطرق الطيفية Uv, FT-IR, HNMR .

الكلمات المفتاحية : اوكساديازول ، قاعدة شف ، ثايازولدين