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To cite this article: Sanaa A Al-Sahib *et al* 2019 *J. Phys.: Conf. Ser.* **1294** 052024

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# Synthesis, Characterization Of Organic Nanoparticles of Oxadiazole Derivative

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**Abstract** .The synthesis oxadiazole derivative 2,5-disubstituted-1,3,4-oxadiazole (3a,3b,3c) was prepared from reaction of N-(4-amino benzene sulphonyl)Morpholipebut-2-enehydrazide with (4-hydroxybenzaldehyde,4-methoxy benzaldehyde,4-ethoxybenzaldehyde) in the presence of lone as catalyst. The structure of (3a,3b,3c) was characterized by using FT-IR , H-NMR and spectroscopy . Nanoparticles of the prepared compounds have been fabricated in aqueous media using re-precipitation method.Characterization of the nano particles (ONPs) have been performed by using UV-VIS spectrophotometer and scanning electron micro scope ( SEM) .The size of the nanoparticales were around 150-200 nm as indicated by (SEM). The maximum of absorption spectrum of the dispersed nanoparticales red shifted by 5nm from the molecules of product in the solution.

**Key words** : Nanoscience , Organic Nanoparticle, Oxadizole derivative , 2,4-disubstituted-1,3,4 oxadizole, Reprecipitation .

## 1. Introduction

Organic nanoparticales (ONPs) are expected to have the potentials them other inorganic and metallic nanoparticales because variability in synthesis and tailoring of organic compound is infinite [1,2] . Thus small molecular organic nano-structures have attracted intense attention as they can offer tunable electronic and optical properties via molecular design [3] .

Oxadiazole derivatives are considered as important organic compounds with have played a significant role in medical and agricultural chemistry [4,5] . Due to their biological and pharmaceutical activates, they have used in drug synthesis [6] .

Researches on (ONPs) , however, are at very beginning and until now , synthetically controlling the size ,shape and applications Nanoscience and Nanotechnology are lying in frontier line of the research works all over the globe, unique , mechanical , electrical and ....etc[7,8] .



In the present work, novel class of oxadiazole derivative has been synthesized . Reprecipitation method was used for used precipitation of organic nanoparticules in water [9] .

Characterization nanoparticules using spectroscopic and microscopic techniques .

## 2. Experimental section

1- The FT-IR spectra were recorded on Perkin-Elmer FT-IR Spectrometer using KBr pellets (  $V_{max}$  in  $cm^{-1}$  ).

2- the  $^1H$ -NMR Spectrometer ( 250 MHz) in  $CDCl_3$  for compound (1) ,  $MDSO-d_6$  for compound (2) and compounds (3a,3b,3c) with TMS as internal standard chemical shift ( $\delta$ ) are reported in ppm.

3- the mass spectra were obtained by using Agilent technology (HP) and MS Model ,5973 Network Mass selective Detector.

4- the reactions were monitored by TLC using Aluminum silica 60 fluorescent plates which were obtained from chemical group of Barcelona ( Spain) Made in EEC.

5- the UV-VIS absorption spectra were measured with a Perkin Elmer lambda 25, UV-VIS spectrophotometer .

6- Electron images were taken using Scanning Electron Microscope (Hitachi S3200 LV) . 1-3 drops of NP solution were drop casted on 0.5 x 0.5 cm piece of glass and then a very thin gold layer was coated using sputtering technique .

### 2.1. Synthesis of compound (E)-ethyl3-((4-(morpholinosulfonyl)phenyl)amino)but-2-enoate (1)

The starting material of N-(4-aminobenzene sulphnyl)morpholine with ethylacetoacetate was synthesized as reported in literature with some modifications ( Cunha , et.al. , 2005) it can be summarized as follow:

Ethyl acetoacetate( 0.02 mole ,2.6 g ,2.53 ml) was added to an ethanolic solution (5 ml) of N-(4-aminobenzene sulphnyl) morpholine (0.01 mole, 2.42 g) in conical flask .

The mixture was stirring and scratching for twenty minutes at room temperature . after completion of reaction , checked by single spot TLC (eluent: petroleum ether/ethyl acetate /methanol 6.5: 1.5:2) .

The light yellow solid was filtered, washed twice with diethyl ether , offering (2.6 g ) of the product. Petroleum ether was added to the mother solution and allowed to cool in freeze, and then (0.156 g ) of the product was precipitated. The product was purified by re-crystallization from ethanol ( yield: 94% ,M.p 181-182 °C  $R_f$ = 0.78).

FT-IR (KBr)  $v_{max}$   $cm^{-1}$  : 324.5(N-H) , 3056(C-H aromatic) , 2975(C-H aliphatic), 1678( C=O ester), 1660( C=O 4 AA), 1604 ( C=C aromatic) , 1275(C-N) , 1133( C-O).

$^1H$ -NMR (250 MHz ,  $CDCl_3$ ) ,  $\delta$  : 1.31(t,3H,O-C-CH<sub>3</sub>) ; 1.95(s,3H, C=C-CH<sub>3</sub>) ; 2.26(s,3H,N-C-CH<sub>3</sub>); 3.1(s,3H,N=CH<sub>3</sub>); 4.16(q,2H,O-CH<sub>2</sub>); 4.74(s,1H,-C=CH); 7.3-7.52(m,4H, Ar-H); 9.42(s,1H,NH-C=C).

MS (m/z): 340 [M + 1]<sup>+</sup> (24), 339 [M]<sup>+</sup> (90), 293 (30), 236(35), 226 (36), 159 (100).

## 2.2. Synthesis of compound (E)-N-(4-(hydrazinyloxy)-4-oxobut-2-en-2-yl)-4-(morpholinosulfonyl)aniline (2)

A mixture of compound (1) (0.02 mole, 2.41g) and hydrazine hydrate (99%) ( 0.015mole, 0.75g, 10.73) in ethanol(25ml ) was refluxed in water-bath for six hours . after completion of reaction , check by single spot TLC(eluent: petroleum ether /ethylacetate/methanol, 6.5:1:5.2).

The excess of solvent was removed by rotatory evaporator. The dark yellow solid was filtered ,washed with diethyl ether and petroleum ether dried and purified by ethanol .

(Yield: 94% , Mp. 110-112 °C Rf= 0.6).

FT-IR (KBr)  $\nu_{\max}$   $\text{cm}^{-1}$  : 3333432, 3327(N-H & NH<sub>2</sub>) , 2989-2915 (C-H aliphatic) , 1665(C=O amide), 1646(C=O 4AA) , 1590( C=C), 1270(C-N).

<sup>1</sup>H-NMR (250 MHz , DMSO-d<sub>6</sub> ) ,  $\delta$  : (s,6H,C=C-CH<sub>3</sub> and N-C-CH<sub>3</sub>) , 2.5(s,2H,NH<sub>2</sub>) , 2.74(s,3H, N-CH<sub>3</sub>). 3.83(s, 1H,NH-C=C), 5.22(s,1H,C=CH), 7.2-7.49(m,4H,Ar-H), 10.28(s,1H,O=C-NH).

MS (m/z): 295 [M]<sup>+</sup> (20), 275 (40), 182 (52), 141(66).

## 2.3. Synthesis of compounds (E)-4-(5-(2-((4-(morpholinosulfonyl)phenyl)amino)prop-1-en-1-yl) -1,3,4-oxadiazol-2-yl)phenol (3a), (E)-N-(1-(5-(4-methoxyphenyl) -1,3,4-oxadiazol -2-yl)prop-1-en-2-yl)-4(morpholinosulfonyl) aniline (3b) and (E)-N-(1-(5-(4-ethoxyphenyl)-1,3,4 -oxadiazol-2-yl) prop-1-en-2-yl) -4- (morpholinosulfonyl) aniline (3c).

A mixture of compound(2) (0.005 mole, 1.205 g) and 4-hydroxybenzaldehyde(0.005mole,0.61g) (or 4-methoxybenzaldehyde 0.005mole,0.65g) (or4-ethoxybenzaldehyde 0,001mmole,0,253 g) was grounded with iodine(0,001 mole, 0.253g) for 15 minutes in a mortar by a pestle .

The completion of the reaction was checked on TLC by using petroleum ether: ethyl acetate: methanol (6.5: 1.5: 2) as solvent system . the ice cold solution of sodium thiosulphate ( 10%) 50 ml was added to the reaction mixture to remove iodine present .

The reddish brown solid that separated out filtered, washed with water., dried and purified by ethanol ( yield 80-85% , Mp. 210-212 °C) , Rf= 0.65 .

FT-IR (KBr) ( $\text{cm}^{-1}$ ) : 3445(broad peak, N-H and O-H)

3a: 1654 (C=O), 1610( C=N) , 1581(C=C), 1257 (C-N), 1158( C-O-C) .

3b: 1660 (C=O), 1618( C=N) , 1580( C=C), 1257(C-N), 1150( C-O-C) .

3c: 1655 (C=O), 1612( C=N) , 1582( C=C), 1257(C-N), 1165( C-O-C).

<sup>1</sup>H-NMR (250 MHz , DMSO-d<sub>6</sub> ) ,  $\delta$  :

**(3a):** 2.42( s,3H,C=C-CH<sub>3</sub>) ; 3.13(s,3H,N-C-CH<sub>3</sub>) ; 3.37(s,3H,N-CH<sub>3</sub>) ; 6.82-7.78(m, 10H,Ar-H and – C=CH); 9.47(s,1H,C=C-NH); 9.94(s,1H,O-H).

MS (m/z): 388 [M]<sup>+</sup> (10), 353 (70), 310 (35), 292(100), 221(12).

## 2.4. Synthesis of Nanoparticles

The re-precipitation method was used for the synthesis of organic nanoparticles. (Mori et al, 2009) Nanoparticles of (3a, 3b, 3c) were synthesized by dissolving (3a, 3b, 3c) in THF (5ml, here THF is called a good solvent), then quickly injecting 100 ml of the 3a/THF, 3b/THF, 3c/THF solution into 10 ml of poor solvent, which is deionized water under an inert atmosphere with vigorous stirring at room temperature. The resulting Nanoparticles solution, after had a clear pale yellow color [10,11].

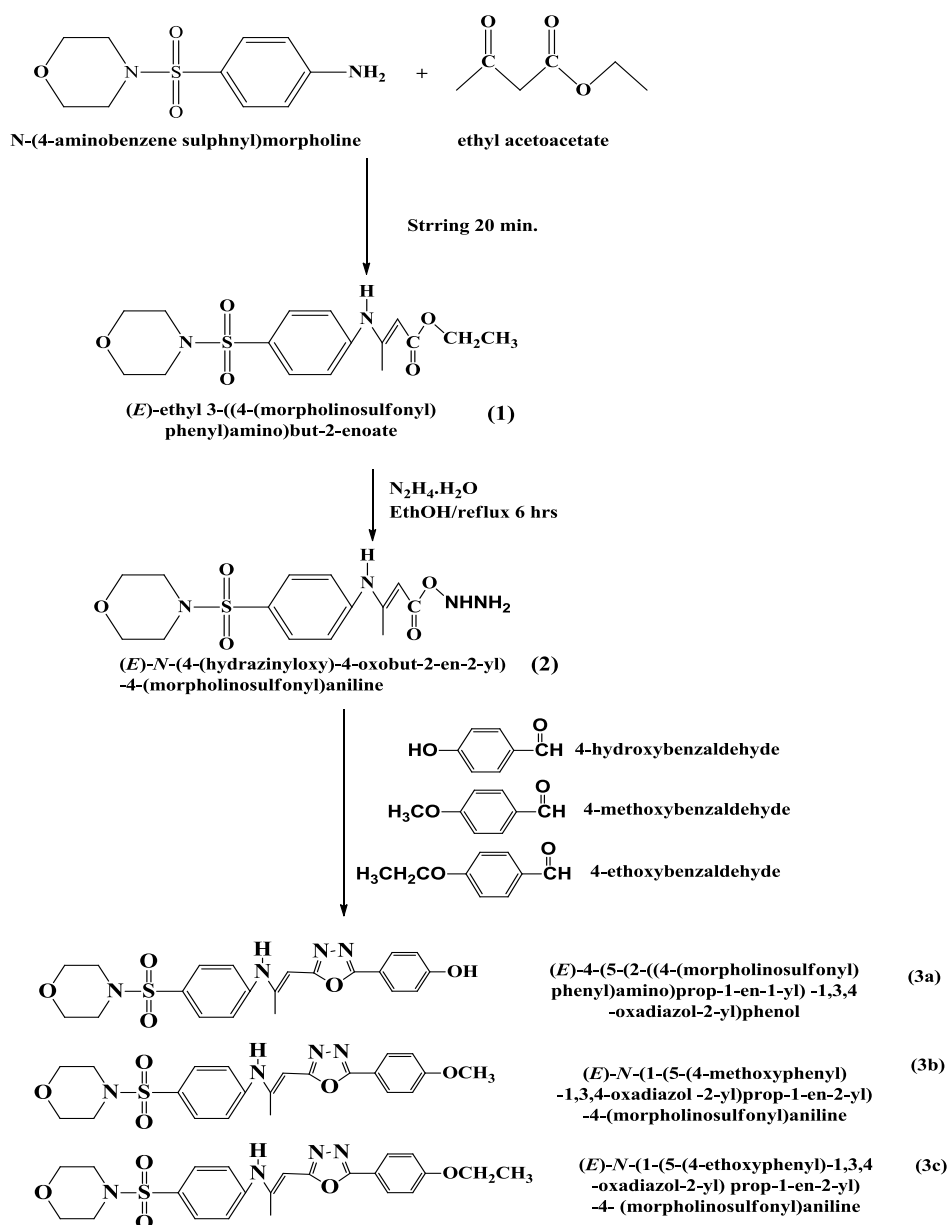


Figure 1. Pathway of the synthesis of oxadiazole derivatives

### 3.Result and Discussion .

The synthetic route of synthesis (3a, 3b, 3c) is shown in [figure 1](#).

In the presence of catalytic amount of iodine molecular in single step with (80-85%) yield for (3a, 3b, 3c) under solvent –free condition using grinding technique as a green method . the specific advantages of this method are rapid and simple work up procedure , high efficiency , and short reaction time , avoiding the use of organic solvents at any stage of the reaction , eco friendly and good yield . short reaction time avoiding the use of organic solvents at any stage of the reaction , eco-friendly.

#### 3.1. Nanoparticles characterization

##### 3.1.1. SEM

The SEM images of the 3a,3b,3c nanoparticles are shown in figure 2 , the nanoparticles are spherical to rod-like shape and the average size is 150 nm. The electronic microscope image of organic nanocrystals was not very clear due to the lower contrast of organic nanoparticles [12,13] .

These nanoparticles were stable in solution in dark room without precipitation at room temperature for at least two weeks, these images confirm the preparation of 3a ,3b, 3c

Nanoparticles via re-precipitation method and the 3a,3b,3c nanoparticles are held together by  $\pi$ -stacking effects and hydrophobic and hydrogen bonds.

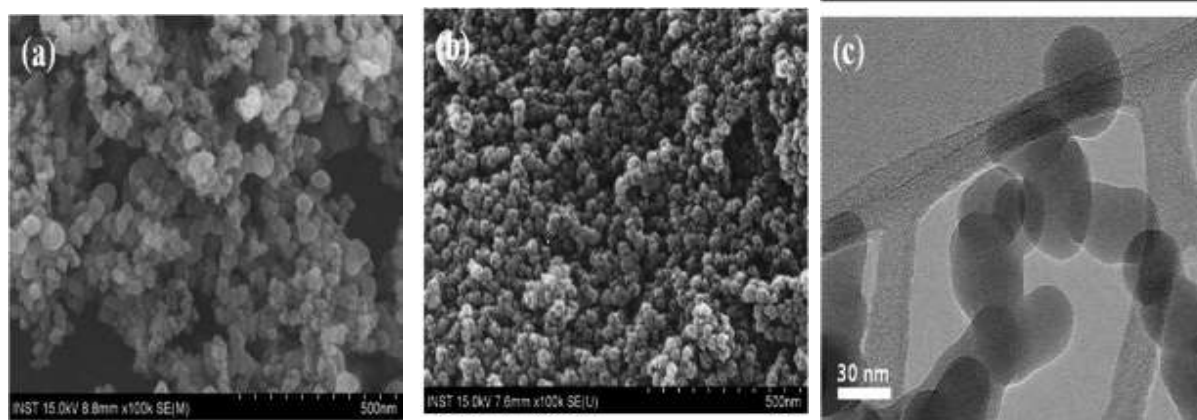


Figure 2 SEM images of the 3a,3b,3c nanoparticles

#### 3.2. Optical properties

The UV-VIS spectra of 3a, 3b, 3c nanoparticles in water are significantly different compared to the spectra of the corresponding 3a,3b,3c solution figure 3 the maximum absorption spectrum nanoparticles solution is about 340 nm which is red shifted by 5 nm from the absorption spectra of the molecule in THF solution by 5nm the rearrangement of molecules in aggregates generally fall into two type (edge-to-edge) interactions which are characterized by red shifts and “ H” (face-to-face) interactions are characterized by blue . the optical spectra suggests the arrangement and interactions in the 3a, 3b, 3c nanoparticles and are well understood to be indicative of electronic coupling of the

chromophores in summary, the spherical and rod like shape of organic nanoparticles might have potential applications in many activities, using in photovoltaic devices and using tag for bio imaging.

Although, organic nanoparticles still in its infancy, but it is promising route in nanotechnology realm [14,15].

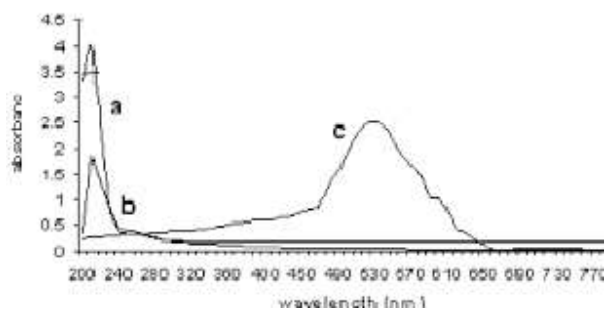


Figure 3 the UV-VIS spectra of 3a, 3b, 3c nanoparticles in water

#### 4. Conclusion

A special class of multifunctional organic molecule of oxadiazole derivatives (3a, 3b, 3c) has been designed and synthesized colloidal spherical and rod like shape of nanoparticles around of 150 nm in aqueous media have been fabricated using re-precipitation method without using any surfactant.

Microscopic characterization showed the size, shape of the nanoparticles spectroscopic characterization explained the optical properties of aggregation of nanoparticles.

In the ultimate goal, medical and environmental application will be tried using these organic nanoparticles.

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