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PREPARATION AND CHARACTERIZATION OF ORGANIC NANOPARTICLES OF NOVEL HETEROCYCLIC COMPOUNDS

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Abstract:
A novel heterocyclic compound,4-((1H-naphtho[1,8-de][1,2,3]triazin-1-yl)sulfonyl)-N-(1-(5-phenyl-1,3,4-oxadiazol-2-yl)prop-1-en-2-yl)aniline(NTOD) was prepared from 4-((1H-naphtho[1,8-de][1,2,3]triazin-1-yl) sulfonyl)- N-(4-(hydrazinyloxy)-4-oxobut-2-en-2-yl) aniline and benzaldehyde in the existence of iodine catalyst, the structure was analyzed by basic content as well as spectroscopic data analysis. By re-precipitation method nanoparticles of the novel synthesized heterocyclic compound NTOD have been prepared in aqueous media. They have been characterized by using UV-Vis spectrophotometer and scanning electron microscope (SEM). SEM shows the size of the nanoparticles were around 70-100 nm. There is head to head alignment (J aggregate) of the molecules of NTOD during the aggregation which was confirmed by the maximum of absorption spectrum of the dispersed nanoparticles is red shifted by 5 nm from the molecular absorption spectra of the NTOD in the solution.

Keywords: Heterocyclic compound,Nanoparticles,Oxadiazoles, Prparation, spectroscopic data analysis.

Introduction

In current era, the research in the field of nanotechnology is undertaken due to its various applications in chemistry, drug delivery, medical science, biomedical, health care, biology, tissue engineering, gene delivery, biotechnology, physics, optics, mechanics, non-linear optical devices, material science, environmental, food industry, space industry and many more [i-v]. In various field novel compounds are produced by using nanoparticles. Numbers of research works are done to produce metal nanoparticles because of their various applications [vi-x]. Many organic reactions have been done by applying metal nanoparticles of Ni, Cu, Ag and Au [xi-xiv].

The growing microbial resistance against the antibiotics and development of resistant strains

also focused researchers towards synthesis nanoparticles [iii,x]. Very few research works was carried out to synthesize Organic nanoparticles (ONPs) in comparison to metal nanoparticles. Synthesis to produce Organic nanoparticles (ONPs) is in their primary stage [xv]. Nitrogen and oxygen containing heterocyclic compound Oxadiazoles derivatives are exposed various commercial uses, industrial uses, biological and pharmaceutical activities [xvi-xx].
In this research article, we discussed the synthesis nanoparticles of a novel heterocyclic compound (NTOD), the characterizing nanoparticles using spectroscopic data analysis and microscopic techniques.

Experimental Section

The contents of carbon, hydrogen and nitrogen were analyzed with a Perkins Elmer (USA) 2400-II CHN analyzer. The melting points were checked using a standard open capillary method and were uncorrected. The IR Spectra were recorded on a Perkin-Elmer FT/IR spectrometer using KBr pellets (ν_{max} in cm^{-1}). The ^1H NMR spectra were recorded NMR spectra were recorded in DMSO with TMS as internal standard on a Bruker spectrometer at 400 MHz chemical shifts (δ) are reported in ppm. The reactions were monitored by TLC , the spots resolved were visualized using UV light.
The UV–Vis absorption spectra were measured with a Beckman DK-2A spectrophotometer. Electron images were taken using Scanning Electron Microscope. 1 to 3 drops of the NP solution were drop casted on 0.5 cm × 0.5 cm piece of glass, and then a very thin gold layer was coated using sputtering technique.

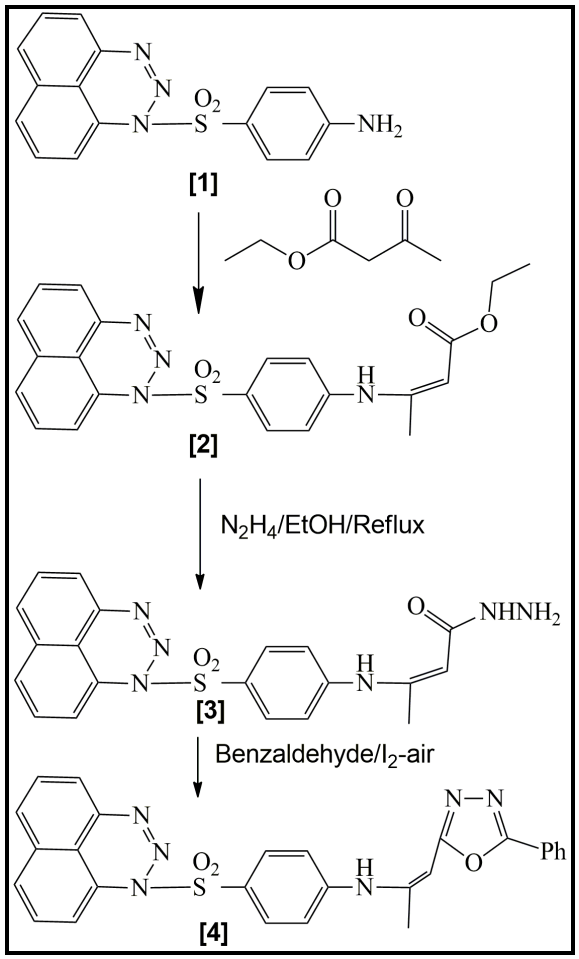

Fig. 1. Synthetic route of **NTOD**

Synthesis of ethyl 3-((4-((1H-naphtho[1,8-de][1,2,3] triazin-1-yl)sulfonyl) phenyl)amino) but-2-enoate (2):

An alcoholic solution of 4-(1H-naphtho[1,8-de][1,2,3]triazin-1-ylsulfonyl)aniline (1) (0.1 mol) mixed with ethyl acetoacetate (0.2 mol) in a conical flask. The mixture was stirring for half an hours at room temperature, the completion of reaction was checked by single-spot TLC, the light yellowish brown solid was filtered, washed thrice with ether. The product was purified by recrystallization from ethanol. yield: 87%; m.p. 172–173°C, For $C_{22}H_{20}N_4O_4S$ (436) Calcd. %C, 60.54;%H,4.62;%N,12.84;%S,7.35,Found% C,60.5;%H,4.6;%N,12.8;%S, 7.3.IR(KBr)ν_{max}(cm^{-1}): 3056 (C-Haromatic), 2975(C-H aliphatic),1360,1155 (SO_2), 1678 (C=O ester), 1590 (C=C),1275(C-N),1133(C-O). ^{1}HNMR (400M Hz):δ1.31(t,3H,O-C-CH_3); 1.95 (s,3H,-C=C-CH_3); 4.83 (s,1H,NH-C=C); 4.16(q,2H,O-CH_2-);4.74(s,1H,-C=CH); 6.48 – 7.99(m,10H, Ar-H).

Synthesis of 4-((1H-naphtho[1,8-de][1,2,3]triazin-1-yl) sulfonyl)-N-(4-(hydrazinyloxy)-4-oxobut-2-en-2-yl)aniline(3):

A mixture of ethyl 3-((4-((1H-naphtho[1,8-de][1,2,3]triazin-1-yl)sulfonyl) phenyl) amino) but-2-enoate (2) (0.1 mol) and hydrazine hydrate (0.15 mol) in ethyl alcohol was refluxed in water-bath for 5-6 hours. The completion of reaction, checked by single-spot TLC. The dark brown solid was filtered, washed with ether, dried and crystallized by ethyl alcohol. Yield: 82%; m.p. 135–136 °C. For: $C_{20}H_{18}N_6O_3S$ (422) Calcd.,% C, 56.86;% H, 4.29;% N, 19.89; %S, 7.59, Found., % C, 56.8;% H, 4.2;% N, 19.8;% S, 7.5.IR (KBr) ν_{max} (cm^{-1}): 3432, 3327 (N-H and NH_2), 2989(C-H aliphatic), 1670 (C=O amide),1590 (C=C), 1360,1155 (SO_2),1274 (C-N). ^{1}H-NMR (400 MHz):2.5 (s,2H,-NH_2); 4.83 (s, 1H, NH-C=C); 1.95 (s, 3H,-C=C-CH_3); 4.74 (s, 1H, -C=CH); 10.28 (s, 1H, O=C-NH); 6.48–7.99 (m, 10H, Ar-H).

Synthesis of 4-((1H-naphtho[1,8-de][1,2,3]triazin-1-yl) sulfonyl)-N-(1-(5-phenyl-1,3,4-oxadiazol-2-yl)prop-1-en-2-yl)aniline (4):

A 4-((1H-naphtho[1,8-de][1,2,3]triazin-1-yl)sulfonyl)-N-(4-(hydrazinyloxy)-4-oxobut-2-en -2-yl) aniline (3) (0.01 mol) and benzaldehyde (0.01 mol) was grounded with iodine (0.002 mmol) for half an hour in a mortar by a pestle. The completion of the reaction was checked on TLC. The ice cold solution of sodium thiosulphate (10%) was added to the reaction mixture to remove iodine present. The Reddish Brown solid that separated out was filtered, washed with water, dried and crystallized by ethyl alcohol. Yield: 78%; m.p. 205-206 °C. For $C_{27}H_{20}N_6O_3S$ (508), Calcd.%C, 63.77; %H, 3.96;% N, 16.53; %S, 6.31,Found. %C, 63.7; %H, 3.9;% N, 16.5; %S, 6.2.IR (KBr) ν_{max} (cm^{-1}): 3445 (broad peak, N-H), 3056 (C-H aromatic), 2975 (C-H aliphatic), 1610 (C=N),1581 (C=C), 1274 (C-N),1158 (C-O-C), 2989-2914 (C-H aliphatic), 1360, 1155 (SO_2).^{1}H-NMR (400 MHz): δ 1.95(s,3H,-C=C-CH_3);6.48-8.04 (m,15H,Ar-H);4.83(s,1H, NH-C=C); 4.74 (s, 1H, -C=CH).

Synthesis of Nanoparticles

The organic nanoparticles was synthesised by re-precipitation method [xxi,xxii]. Nanoparticles of **NTOD** were synthesized by dissolving **NTOD** in THF (5 mM) then quickly injecting 100 µL of the **NTOD/THF** solution into 10 mL of poor solvent, which is deionized water under an inert atmosphere with vigorous stirring at room temperature. The resulting NP solution, after had a clear pale yellow color.

Results and Discussion

Synthesis of 4-((1H-naphtho[1,8-de][1,2,3]triazin-1-yl)sulfonyl)-N-(1-(5-phenyl-1,3,4-oxa-diazol -2-yl)prop-1-en-2-yl) aniline (4) was synthesized by reaction of 4-((1H-naphtho [1,8-de] [1,2,3] triazin-1-yl)sulfonyl)-N-(4-(hydrazinyloxy)-4-oxobut-2-en-2-yl) aniline (3) and benz-aldehyde in the presence of catalytic amounts of iodine molecular in a single step with (78%) yield under solvent-free conditions using grinding technique as a green method. The synthetic scheme of **NTOD** is shown in Figure 1. 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, ecofriendly and good yield.

The SEM images of the NTOD nanoparticles are spherical to rod-like shape; the average size is 80 nm. The electronic microscope image of organic nanocrystals was not very apparent due to the lower contrast of organic nanoparticles. These nanoparticles were stable in solution in dark room without precipitation at room temperature for at least 2 weeks. These images validate the preparation of NTOD nanoparticles via re-precipitation method and the NTOD nanoparticles are held together by π-stacking effects and hydrophobic and hydrogen bonds.

The UV-Vis spectra of NTOD nanoparticles in water are considerably dissimilar contrasted to the spectra of the corresponding NTOD solutions. The maximum absorption spectrum nanoparticle solution is about 340 nm which is red shifted by 5 nm from the absorption spectra of the molecule in THF solution by 5 nm.

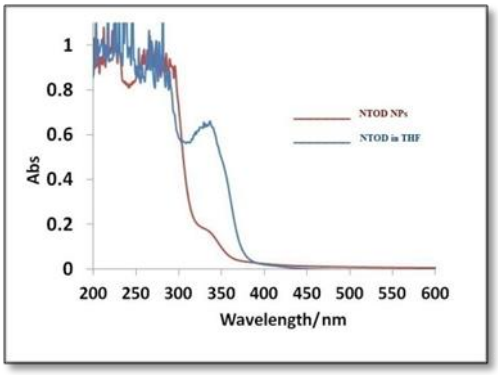

Fig. 2. UV-Vis spectra of NTOD

The rearrangement of molecules in aggregates usually fall into two types, ”J”(edge-to-edge) interactions which are characterized by red shifts and “H” (face-to-face) interactions are characterized by blue shifts. The optical spectra proposed the arrangement and interactions in the **NTOD** nanoparticles and are well understood to be indicative of electronic coupling of the chromophores [xxiii].

In outline, the spherical and rod like shape of organic nanoparticles might have probable purposes in many fields, like; showing biological activities, using in photovoltaic devices, and many others.

Conclusion

A novel heterocyclic compound, 4-((1H-naphtho[1,8-de][1,2,3]triazin-1-yl)sulfonyl)-N-(1-(5-phenyl-1,3,4-oxadiazol-2-yl)prop-1-en-2-yl)aniline **(NTOD**) has been designed and synthesized. Colloidal spherical and rod like shape of nanoparticles in aqueous media have been synthesized using reprecipitation method without using any surfactant. The optical properties of the aggregation of nanoparticles were characterized by microscopic characterization showed the size, shape of the nanoparticles, spectroscopic characterization.

In the last object, medical and environmental application will be attempted using these organic nanoparticles.

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