Original article

Synthesis of Some O-Cresol Mannich Bases and Calculation of Optical Properties

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ARTICLE INFO

Article history:

Received 2020 October 19th
Reviewed 2020 November 18th
Accepted 2020 December 14th

Keywords:

O-Cresol Mannich, phenolic Mannich, active hydrogen compound, Optical properties

Abstract

This study aimed to synthesize two types of phenolic Mannich bases and to calculate some of their optical properties. A general synthesis strategy was adopted: the active hydrogen compound, formalin and a secondary amine were mixed in ethanol for different intervals to afford the final products. In this way, the following Mannich bases were synthesized (1-[(piperidin-1-yl) methyl] naphthalen-2-ol) and (3-(diethyl amino) naphthalen-2-yl acetate). The optical properties. e.g. the absorption, absorption coefficient extinction coefficient, refractive index and energy band gap were calculated for ((1-[(piperidin-1-yl) methyl] naphthalen-2-ol) and (3-(diethyl amino) naphthalen-2-yl acetate)) samples by using spectrophotometer measurements of the transmittance and reflectance at normal incidence in the spectral range 200–500 nm. The two Mannich bases illustrated different values for the calculated parameters (absorption, absorption coefficient, extinction coefficient, refractive index and energy band gap). The differences are related to the nature of Mannich base.

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Introduction

The development of new antimicrobial agents will remain an important challenging task for medicinal chemist [Malhotra, *et al*, 2012]. So, there is an urgent need for identification of novel lead structure for the designing of new, potent and less toxic agents [Murphy *et al.* 2007]. Mannichreaction is a three -component condensation involving active hydrogen compound, formaldehyde and a secondary amine [Sujith, et al. 2009]. As shown in scheme 1, the Mannich reaction product (the Mannich base) has the N-atom of the nitrogen functionality linked to the substrate R through a methylene group. This transformation was first discovered by Carl Mannich in 1912, when he treated a salicylic antipyrine pharmaceutical preparation and urotropine with acid [Tramontini. 1973].

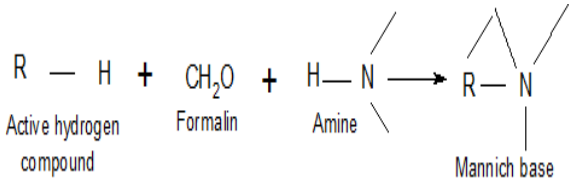

Figure (1) Mannich reaction

It is believed that the Mannich base functional group can increase the lipophilicity of parent amines and amides, which results in the enhancement of absorption through bio-membranes [Abuo-Rahma, *et al*. 2009]. The lipophilicity of Mannich bases enables them to cross bacterial and fungal membranes [Malhotra, *et al*, 2012].The chemistry of Mannich bases, first studied by Carl Mannich has been the subject of investigations by an ever increasing number of researchers, several studies which appeared before 1960 together with books by Reichert, Hellman and Optimize, provide an excellent coverage on practically the entire chemistry of Mannich bases up to 1960 [Tramontini. 1973].Mannich bases have gained importance due to their application in pharmaceutical chemistry. Previous studies have demonstrated that Mannich bases offer a wide range of biological activities [6]. They have been encountered with antibacterial [Bekiram *et al*. 2008], anticancer [Holla *et al*. 2003], analgesic andanti-inflammatory [Gokee *et al*. 2005], antimalarial [Gokee et al. 2004], antiviral [Sriram*et al*. 2005], and CNS depressant activities [Knabe *et al*. 1983].

Material and methods

A general synthesis strategy was adopted; the active hydrogen compound, formalin and a secondary amine were mixed in ethanol for different intervals to afford the final products. In this way the following Mannich bases were synthesized (1-[(piperidin-1-yl) methyl] naphthalen-2-ol) and (3-(diethyl amino) naphthalen-2-yl acetate). - Synthesis of Mannich base1, formalin (3.2 g, 20 mmol), β- naphthol (2.88 g, 20 mmol) and piperidine (1.68 g, 20 mmol) in 20 ml ethanol were left at room temperature for 7 days. Removal of the solvent under reduced pressure gave the Mannich base.-Synthesis of Mannich base 2**:**Formalin (3.2 g, 20 mmol), β- naphthol (2.88 g, 20 mmol) and diethylamine (1.46g, 20 mmol) in 20 ml ethanol were left at room temperature for 7 days. Removal of the solvent under reduced pressure gave the Mannich base-1. (1.78g) of Mannich base was suspended in 5 ml (3M) NaOH solution. Crushed ice was added followed by 2.48 ml of acetic anhydride. The mixture was vigorously shacked for 60 seconds. The acetate separated after acidification by the addition of hydrochloric acid. The acetyl derivative was collected and recrystallized from dilute ethanol.The optical measurements of (1-[(piperidin-1-yl) methyl] naphthalen-2-ol) and (3-(diethyl amino) naphthalen-2-yl acetate) samples were carried out at room temperature using Min1240 Spectrophotometer in the wavelength range from 200 to 500 nm.

Results

A targeted series of phenolic Mannich bases1 and 2 were synthesized via a general procedure. The optical properties of the final products were elucidated by a combination of spectral techniques

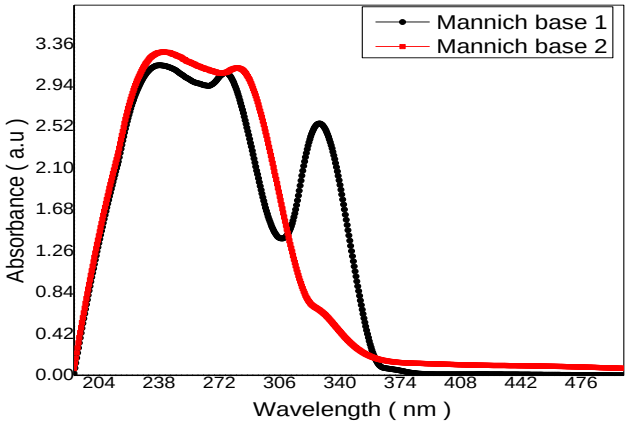

Figure (1) the Absorbance spectrum of compound 1and 2

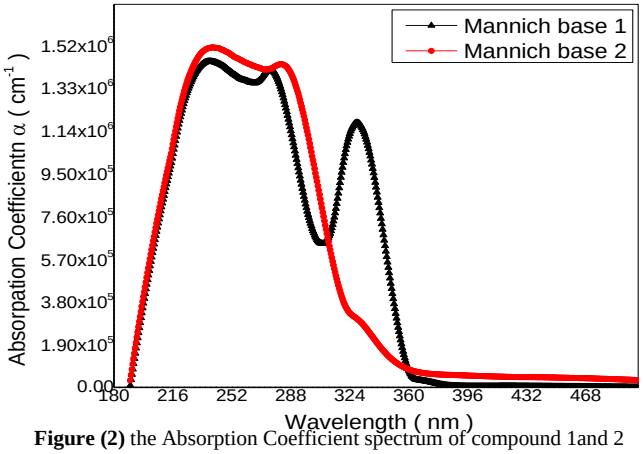

Figure (2) the Absorption Coefficient spectrum of compound 1and 2

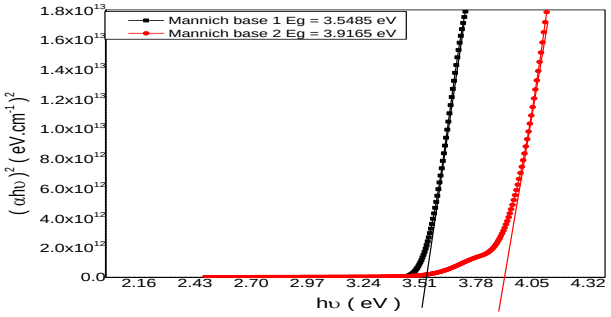

Figure (3) the energy band gap spectrum of compound 1 and 2

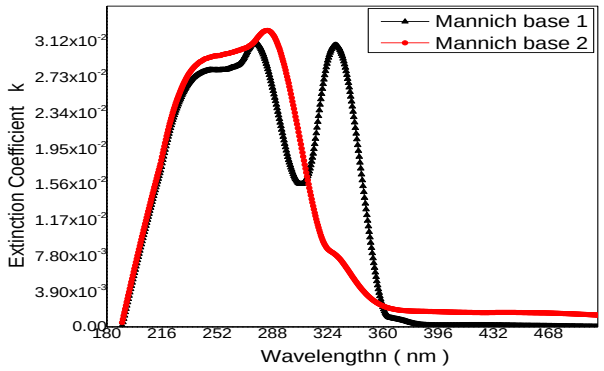

Figure (4) the Extinction Coefficient spectrum of compound 1and 2

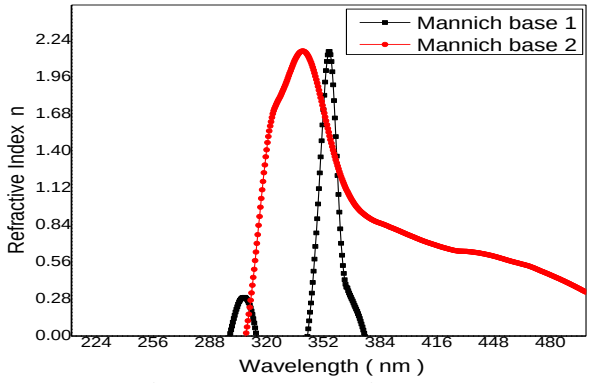

Figure (5) the refractive index spectrum of compound 1and 2

Discussion

The relation between absorbance and wave lengths, they found the behavior of curves is the same for targeted series of phenolic Mannich bases1 and 2studied using UV-VS min 1240 spectrophotometer,

Figure (1) shows the spectrum of base I showed λ_{max} (MeOH) 240.5, 277.5, 329.2 nm, and the spectrum of base 2 showed λ_{max} (MeOH) 239 nm.

The absorption coefficient (α) of the prepared samples also of the concentration were found from the following relation $\alpha = 2.303\ A/t$. where (A) is the absorbance and (t) is the optical length on the samples. Figure (2) shows the plot of (α) with wavelength (λ) of targeted series of phenolic Mannich bases1 and 2, which obtained that the value of α equal $1.521x10^6$ cm^{-1} for Mannich bases2 sample at 240 nm in the U.V region, this means that the transition must corresponding to a direct electronic transition, and the properties of this state are important since they are responsible for electrical conduction. Also, fig(2) shows that the value of (α) for the Mannich bases1sample decrease ($1.521x10^6$ cm^{-1} at the same wavelength) .The optical energy gap (Eg) has been calculated by the relation $(\alpha h\upsilon)^2 = C(h\upsilon - Eg)$ where (C) is constant. By plotting $(\alpha h\upsilon)^2$vs photon energy (hυ) as shown in fig(3) for targeted series of phenolic Mannich bases1 and 2 sample . And by extrapolating the straight thin portion of the curve to intercept the energy axis , the value of the energy gap has been calculated .In fig (3) the value of (Eg) of sample treatment of Mannich bases1 obtained was (3.5485) eV , which is the value of(Eg) was increased from (3.9165) eV for Mannich bases2 sample . The increasing of (Eg) related to decrease in concentration of samples number of wavelength of (λ_{max} (MeOH)) in the spectrum as show in figure (1).

Extinction coefficient (K) was calculated using the relation $K = \lambda\ \alpha\ /4\ \pi$. The variation at the (K) values as a function of (λ) are shown in fig (4) for targeted series of phenolic Mannich bases1 and 2 samples for the studied and it is observed that the spectrum shape of (K) as the same shape of (α). In fig (4) obtained the value of (K) at the (180 - 500 nm) region was depend on the samples treatment method , where themaximumvalue of (K) at 285 nm for Mannich bases2 sample is $3.25x10^{-2}$ while the maximum value for

treatment Mannich bases1 sample at 330 nm wavelength equal $3.1x10^{-2}$.

The refractive index (n) is the relative between speeds of light in vacuum to its speed in material which does not absorb this light. The value of n was calculated from the equation

$$n = \left[\left(\frac{1+R}{1-R}\right)^2 - (1+k^2)\right]^{\frac{1}{2}} + \frac{1+R}{1-R}$$

Where (R) is the reflectivity. The variation of (n) vs. (λ) for all samples was targeted series of phenolic Mannich bases1 and 2 is shown in figure (5).

In Figure (5) the relationship of sample targeted series of phenolic Mannich bases1 and 2 which shows that the maximum value of (n) is (2.16) for Mannich bases1 sample at the wavelength (360nm). Also we can show that the maximum value of (n) for the Mannichbases1 sample equal (2.16) at (340 nm) wavelength.

Conclusions

- The spectrum of base I showed λ_{max} (MeOH) 240.5, 277.5, 329.2 nm, and the spectrum of base 2 showed λ_{max} (MeOH) 239 nm. The value of (Eg) of sample treatment of Mannichbases1 obtained was (3.5485) eV, which is the value of (Eg) was increased from (3.9165) eV for Mannich bases 2 sample.
- The increasing of (Eg) related to decrease in concentration of samples number of wavelength of (λ_{max} (MeOH)) in the spectrum.
- The maximum value of (n) is (2.16) for Mannich bases1 sample at the wavelength (360 nm), and (2.16) at (340 nm) wavelength for the Mannich bases1 sample equal.

References

Abuo-Rahma, G. E. D. A., Sarhan, H. A., & Gad, G. F. (2009). Design, synthesis, antibacterial activity and physicochemical parameters of novel N-4-piperazinyl derivatives of norfloxacin. Bioorganic & medicinal chemistry, 17(11), 3879-3886.

Bekiram, O. and Bektas, H. (2008): Molecules, 13, 2126-2135, Dol: 10.3390"molecules" 3092126.

Gokee,E.,Bakir,G.,Sahin,M.F.,Kupeli,E.,Yesilada,E.(2005): Synthesis of new Mannich bases of aryl pyridazinones as analgesic and anti-inflammatory agent.Arzenim.Forsch,55,318-325.

Holla, B. S., Shivananda, M. K. ,Shenoy, M.. S., Antony, G. (1998). Synthesis and characterization of some Mannich bases carrying halo phenyl furyl moieties as promising anti-bacterial agents. Farmaco, 53, 531-535.

Holla, B.S.,Shivananda, M. K.,Veerendra, B., Poojary, B.(2003): Synthesis Characterization and anti-cancer activity studies on some Mannich bases derived from 1,2,4 tri azoles. Eur. J. Med. Chem., 38,759-767.

Knabe, J.,Buch, H.P.,Schmitt,W.(1983): Derivatives of barbituric acid cytostatic and CNS activities of chiral barbiturate Mannichbases.*Arch.pharm.chem.chem.life sci*.,316,1051-1053

Lopes, F., Capela, R., Goncaves, J. O., Horton, P. N., Hursthouse, M. B., Iley, J., Casimiro, C. M., Bom, J., Moreire, R. (2004. Amidomethylation Activities of isatin Mannich bases. *Med. Chem. Res*,14,11-28.of amodigquine anti-malarial N-Mannich base derivatives.*Tetrahedron Lett*,45,7663-7666.

Malhotra, M., Sharma, R., Sanduja, M., Kumar, R., Jain, J., and Deep, A. (2012). Synthesis, characterization and evaluation of Mannich bases as potent antifungal and hydrogen peroxide scavenging agents. Acta. Poloniae. Pharmaceutica. Drug Research, 69(2), 355-361.

Murphy, S. T., Case, H. L., Ellsworth, E., Hagen, S., Huband, M., Joannides, T., and Starr, J. (2007). The synthesis and biological evaluation of novel series of nitrile-containing fluoroquinolones as antibacterial agents. Bioorganic & medicinal chemistry letters, 17(8), 2150-2155.

Sriram, D., Bal, T.R., Yogeesswari, P.: (2005). Synthesis, anti-viral and anti-bacterial

Sujith, K. V., Rao, J. N., Shetty, P., &Kalluraya, B. (2009). Regioselective reaction: synthesis and pharmacological study of Mannich bases containing ibuprofen moiety. European journal of medicinal chemistry, 44(9), 3697-3702.

Tramontini, M.,, (1973) Synthesis, 63, 702-720.