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SYNTHESIS, CHARACTERIZATION AND INVESTIGATION OF SECOND- HARMONIC GENERATION EFFICIENCY OF AZETIDINONE DERIVATIVES ENCOMPASSING 3-NITRONAPHTHO[2,1-b]FURAN

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ABSTRACT

In the last few decades, nonlinear optical materials are getting attention in the field of optical data storage, telecommunication, second harmonic generation (SHG) and optical signal processing, etc. In the present work, we are reporting the synthesis and non-linear optical (NLO) property of new naphthofuran derivatives. Second harmonic generation (SHG) efficiency has been observed in the target molecules. Ethyl 3-nitronaphtho[2,1-b]furan-2-carboxylate **2** has been synthesized from ethyl naphtho[2,1-*b*]furan-2-carboxylate **1**. This nitro product on reaction with hydrazine hydrate formed 3-nitronaphtho[2,1-b]furan-2-carbohydrazide **3**. Various Schiff's bases i.e. 3-nitro-N^1 (aryl-methylene)-substituted-naphtho[2,1-*b*]furan-2-carbohydrazides **4(a-g)** were obtained by treating hydrazide **3** with different aromatic aldehydes. These Schiff bases on reaction with chloro acetyl chloride in presence of triethylamine as catalyst in dioxane yielded 3-nitro-N-(3-chloro-2-oxo-substituted-phenyl-azetidine-1-yl)naphtho[2,1-b]furan-2-carboxamides **5(a-g)**. The newly synthesized compounds were characterized by analytical and spectral studies. The second harmonic generation (SHG) efficiency of these compounds was measured by powder technique using PROLAB 170 laser. Among tested compounds three naphthofuran derivatives showed NLO property. Compounds, **5a** exhibited NLO property with SHG conversion efficiency 0.12 times that of potassium dihydrogen orthophosphate (KDP), compound **5c** exhibited NLO property with SHG conversion efficiency 0.42 times that of KDP, compound **5e** exhibited NLO property with SHG conversion efficiency 0.21 times that of KDP.

Key words: Non-linear optical property, Naphtho[2,1-b]furan, Azetidinones, Second harmonic generation.

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INTRODUCTION

Nonlinear optics (NLO) is at the forefront of current research because of its importance in providing the key functions of frequency shifting optical modulation, optical switching, optical logic, and optical memory for the emerging techniques in areas such as telecommunications, signal processing, and optical interconnections[1-3]. Organic materials have been of particular interest because the nonlinear optical response in this broad class of materials is microscopic in origin, offering an opportunity to use theoretical modeling coupled with synthetic flexibility to design and produce novel materials[4-6].

Organic NLO materials have a very large nonlinear susceptibility, which are in many cases several orders of magnitude higher than that of inorganic crystals such as $LiNbO_3$, $KNbO_3$ and potassium dihydrogen phosphate (KDP)[7,8]. Methyl-para-hydroxy benzoate (MHB) is an organic NLO material. In the study, it is reported that the second harmonic generation (SHG) efficiency of MHB crystal was 40 times that of urea[9].

This expectation explains extensive search for better NLO materials among organic crystals. Second harmonic generation (SHG) conversion efficiency was investigated to explore the NLO characteristics of this material using Kurtz and Perry method and it was found that the SHG conversion efficiency is about 90% of that of the standard KDP crystals[10].

Organic materials are significantly used as non-linear optical (NLO) materials because of their optical transparency[11]. These non-linear optical materials are of particular importance in the development of light based technology for communication and computing[12]. Thus organic crystals have been shown to have potential applications in nonlinear optics[13-21]. Several research papers have been published in recent years describing both synthesis and optical properties of different organic molecules[22-26].

Survey of literature revealed that heterocyclic compounds have not been explored for NLO studies to the required extent. Especially no such study has been undertaken for exploring naphthofuran derivatives. Initiation has been taken in this direction in our laboratory and some symmetrical and unsymmetrical azines encompassing naphthofuran have been found to exhibit potential NLO activity[27,28].

EXPERIMENTAL

Materials and methods

Melting points were recorded in open capillary tubes and are uncorrected. IR (cm^{-1}) were recorded in KBr on FT-IR (Research spectrometer) Shimadzu 8201 PC (4000-400 cm^{-1})

and NMR on Bruker DRX-300 (300 MHz-FT-NMR with low and high temperature facility-90° to + 80°C). Standard chemical shifts are given in δ ppm values. The compounds were checked for their purity by TLC on silica gel plates using chloroform and ethyl acetate of varying polarities and spots were located by iodine vapour.

Synthesis of ethyl 3-nitronaphtho[2,1-b]furan-2-carboxylate (2)

A cooled nitrating mixture of conc. HNO_3 and conc. H_2SO_4 (1:2, 15 mL) was added very slowly to a cooled solution of ester **1** (2.4 g, 0.01 mol) in glacial acetic acid (4 mL) and the mixture was stirred for about 30 mins at 0 to 15°C. The stirring was continued for 2 hr and the reaction mixture was poured on to crushed ice. The product that separated as solid, was collected, dried and recrysatlised from aqueous ethanol.

Synthesis of 3-nitronaphtho[2,1-b]furan-2-carbohydrazide (3)

A mixture of ethyl 3-nitronaphtho[2,1-*b*]furan-2-carboxylate **2** (2.55 g, 0.01 mol) and hydrazine hydrate (2.5 mL, 99%) in ethanol (10 mL) was heated under reflux for 5 hr, cooled to room temperature and the solid thus separated was filtered, washed with ethanol and recrystallised from aqueous DMF to obtain the product.

Synthesis of 3-nitro-N^1 (aryl-methylene)-substituted-naphtho [2,1-b]furan-2-carbohydrazides (4a-g)

To a solution of 3-nitronaphtho[2,1-*b*]furan-2-carbohydrazide **3** (0.42 g, 0.001 mol) in DMF (50 mL), aryl aldehydes (6 mL) were added, the mixture was refluxed for 5 hr, and then poured into ice-cold water. The product that separated as solid was filtered, dried, and recrystallised from aqueous DMF.

Synthesis of 3-nitro-N-(3-chloro-2-oxo-substituted-phenyl-azetidine-1-yl)naphtho [2,1-b] furan-2-carboxamides (5a-g)

A solution of chloro acetyl chloride (0.6 mL, 0.0055 mol) in dioxane (10 mL) was cooled to -10°C using ice-salt bath and kept for stirring. To this, triethyl amine (0.5 g, 0.005 mol) was added drop wise maintaining the temperature below 0°C, while white solid separated out. To this reaction mixture solution of 3-nitro-N^1 (aryl-methylene)-substituted-naphtho [2,1-b]furan-2-carbohydrazides **4a-g** (0.0025 mol) in dioxane (10 mL) was added drop wise regulating the temperature less than 0°C with stirring. After the addition was over the reaction mixture was refluxed for 16 hr. The reaction mixture was poured into ice cold water. The solid that separated out was filtered dried and recrystallised from dioxane.

The sequence of reactions for the synthesis of azetidinones is depicted in **Scheme 1**.

The physical and analytical data of the compounds is presented in Table 1.

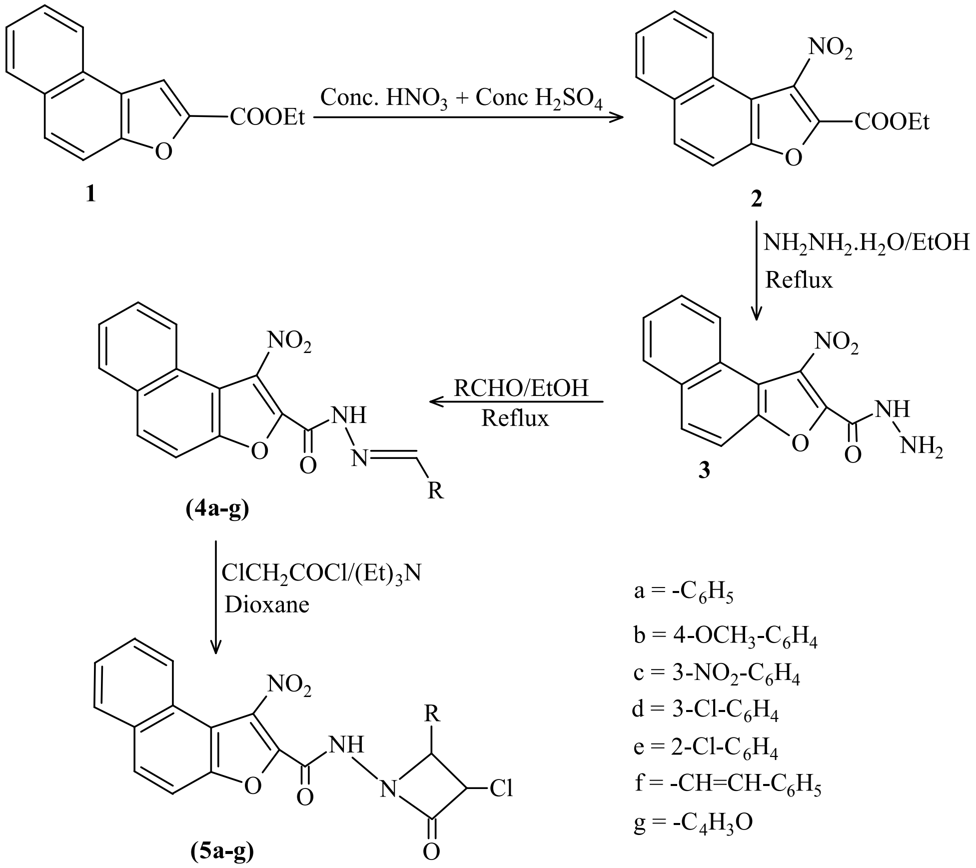
Table 1: Physical and analytical data of the synthesized compounds

Compd.	R	M.P. (^{0}C)	Yield (%)	Mol. formula	Found (Cal.) %		
					C	H	N
5a	-C_6H_5	>250	24.24	$C_{22}H_{16}N_3O_6Cl$	58.20 (58.21)	3.51 (3.52)	9.23 (9.26)
5b	4-$OCH_3C_6H_4$	>250	29.41	$C_{23}H_{16}N_3O_6$ Cl	59.28 (59.29)	3.41 (3.43)	8.97 (9.02)
5c	3-$NO_2C_6H_4$	180	46.71	$C_{22}H_{13}N_4O_7Cl$	54.93 (54.96)	2.81 (2.70)	11.64 (11.65)
5d	4-Cl-C_6H_4	110	26.01	$C_{22}H_{13}N_3O_5Cl_2$	56.13 (56.17)	2.74 (2.76)	3.72 (3.75)
5e	2-Cl-C_6H_4	101	52.94	$C_{22}H_{13}N_3O_5Cl_2$	56.14 (56.17)	2.75 (2.76)	3.73 (3.75)
5f	-CH=CH-C_6H_5	104	26.47	$C_{24}H_{16}N_3O_5Cl$	62.38 (62.40)	3.42 (3.45)	9.07 (9.10)
5g	C_4H_3O	>250	70.96	$C_{20}H_{12}N_3O_6Cl$	56.38 (56.40)	2.81 (2.82)	9.85 (9.87)

Nonlinear optical studies-powder SHG measurement

Kurtz and Perry powder method is an important tool for researchers searching for organic/semi organic/inorganic NLO materials. The experimental set up used in the present investigation was similar to the generic one devised by Kurtz.

The study of nonlinear optical conversion efficiency of naphthofuran derivatives was carried out using the experimental set up of Kurtz and Perry[29]. PROLAB-170 laser of fundamental wavelength 1064 nm was used as the source of light for second harmonic generation (SHG) experiment. The beam with a diameter 8 mm and pulse of width 10 ns with repetition rate of 10 Hz were used. The laser was passed through a couple of high energy laser mirrors (Melles Griot, 99.9% reflection) and a long pass colored glass filter (RG 645, to reject the light from the flash lamp of laser) before be focused. The energy of the laser beam was kept at 1.60 mJ/pulse. The incident beam power was measured using a power meter (Scientech Vector H410). The beam was focused into a glass capillary, using a converging lens of 200 mm focal length. The incoherently scattered SH protons were collected in the transeverse direction using a combination of a monochromator (Triax 550, Jobin Yvon, 0.024 nm resolution, 1 mm entrance and 0.15 mm exit slit widths) and a photomultiplier tube with a power supply 2 KV/AMP. The second harmonic signal was then sampled, averaged over 512 shots and was recorded in a digital storage oscilloscope Tektronix TDS 3052 B. The powder sample with a uniform particle size was packed in a capillary of uniform bore and exposed to laser radiations. The generation of second harmonics was confirmed was confirmed by the emission of green light. The amplitude of the SHG output voltage was measured using photomultiplier and digitalizing oscilloscope assembly. A sample of potassium dihydragen phosphate (KDP), also powdered to the same particle size as the experimental sample was used as a reference material for the present measurement. The second harmonic generation (SHG) efficiency of these compounds was measured by powder technique PROLAB-170 laser with beam energy 1.6 mJ/pulse. The measured SHG values are listed in Table 3.



a = $-C_6H_5$
b = $4-OCH_3-C_6H_4$
c = $3-NO_2-C_6H_4$
d = $3-Cl-C_6H_4$
e = $2-Cl-C_6H_4$
f = $-CH=CH-C_6H_5$
g = $-C_4H_3O$

Scheme 1

RESULTS AND DISCUSSION

The azetidinones **(5a-g)** were selected for NLO studies because of the following reasons:

- They provide basic requirement of conjugated π system in the form of naphtho[2,1-b]furan ring along with two non bonded pairs of electrons available with oxygen atom of furan moiety.
- The presence of two carbonyl groups and nitro group imparts polarity in the molecules due to electron withdrawing nature.
- The chlorine atom present in the ring generates additional polarity due to its inductive effect.
- In addition substitution at C-4 of azetidinone nucleus by various aromatic rings with electron donating and electron withdrawing groups gives versatility to study NLO behavior of the compounds.

The carbohydrazide **3** was treated with various substituted aromatic aldehydes in refluxing ethanol to obtain corresponding Schiff's bases, 3-nitro-N^1 (aryl-methylene)-substituted-naphtho[2,1-b]furan-2-carbohydrazides **(4a-g)** in good yield. The structures of the Schiff's bases **(4a-g)** were established by IR and NMR spectral data. The IR spectrum of compound **4b** exhibited a band at 1653 cm^{-1} due to carbonyl group as expected of Schiff bases. In ^1H NMR spectrum of **4b** a singlet integrating for three protons due to $–OCH_3$ at δ 3.8, multiplet between δ 7.0 and 9.6 integrating for eleven protons (ten aromatic protons and one –CH proton) and D_2O exchangeable singlet at δ 11.6 due to –NH proton were observed.

Synthesis of 3-nitro-N-(3-chloro-2-oxo-substituted-phenyl-azetidine-1-yl)naphtho [2,1-b]furan-2-carboxamides **5(a-g)** was accomplished by the reaction between 3-nitro-N^1 (aryl-methylene)-substituted-naphtho[2,1-b]furan-2-carbohydrazides **(4a-g)** with chloro acetyl chloride in presence of triethyl amine in dioxane. The structure of **5a** was confirmed by elemental analysis and spectral studies. The IR spectrum of **5b** exhibited sharp absorption bands at 1716 cm^{-1} due to amide carbonyl group and at 1679 cm^{-1} due to carbonyl group of β-lactam ring. The broad NH absorption band appeared at 3000-3400 cm^{-1}. ^1H NMR spectrum of **7b** was recorded using DMSO-d_6 as solvent. It showed a singlet for three protons at δ 3.8 due to OCH_3 group. A multiplet at δ 7.0-8.9 integrating for twelve protons was observed, and this has been attributed to ten aromatic and CHPh and –CHCl protons. The CONH proton appeared as a singlet, downfield at δ 12.2 (D_2O exchangeable). The structure of **5b** was confirmed by its mass spectral analysis. No molecular ion peak was observed at m/z 465.5 corresponding to its molecular weight. This fact indicates less stability of molecular ion, which undergoes immediate fragmentation to show peaks at 389, 311, 285, 277, 139, which were in accordance with expected fragmentation pattern.

The structures of the compounds **4a**, **4 c-g**, **5a** and **5c-g** have been confirmed by their IR ^{1}H NMR spectral data, which has been presented in Table 2.

Table 2: IR and ^{1}H NMR data of the synthesized compounds

Comp.	Ar	IR (KBr) cm^{-1}		^{1}H NMR δ in ppm
		C=N	C=O	
4a	C_6H_5	1585	1678	δ 7.1-8.5 (m, 11H, ArH), δ 8.6 (s, 1H, NCH), δ 9.5 (s, 1H, NHCO)
4c	3-NO_2-C_6H_4	1598	1675	δ 7.2-8.6 (m, 10 H, ArH), δ 8.8 (s, 1H, NCH), δ 10.5 (s, 1H, NHCO)
4d	4-Cl-C_6H_4	1610	1680	δ 7.5-8.6 (m, 10H, ArH), δ 8.9 (s, 1H, NCH), δ 10.0 (s, 1H, NHCO)
4e	2-Cl-C_6H_4	1620	1690	δ 7.3-8.3 (m, 10 H, ArH), δ 8.8 (s, 1H, NCH), δ 10.6 (s, 1H, NHCO)
4f	CH=CH-C_6H_5	1617	1685	δ 7.0-8.4 (m, 11H, ArH), δ 8.7 (s, 1H, NCH), δ 10.4 (s, 1H, NHCO)
4g	Furfural	1609	1685	δ 7.0-8.4 (m, 9H, ArH), δ 8.6 (s, 1H, NCH), δ 10.3 (s, 1H, NHCO)
5a	-C_6H_5	1585	1678	δ 7.0-8.7 (m, 13H, 11 ArH + CHAr + CHCl), δ 12.6 (s, 1H, NHCO)
5c	3-$NO_2C_6H_4$	1700	1675	δ 7.1-8.7 (m, 12H, 10 ArH + CHAr + CHCl), δ 11.9 (s, 1H, NHCO)
5d	4-ClC_6H_4	1725	1656	δ 7.1-8.5 (m, 12H, 10 ArH + CHAr + CHCl), δ 12.6 (s, 1H, NHCO)
5e	2-ClC_6H_4	1726	1660	δ 7.2-8.6 (m, 12H, 10 ArH + CHAr + CHCl), δ 12.8 (s, 1H, NHCO)
5f	-CH=CH-C_6H_5	1609	1685	δ7.0-8.4 (m, 15H, 11 ArH + CHAr + CHCl + 2H, CH=CH), δ 11.3 (s, 1H, NHCO)
5g	-C_4H_3O	1679	1638	δ 7.2-8.4 (m, 11H, 9 ArH + CHAr + CHCl), δ 12.8 (s, 1H, NHCO)

Table 3: Comparison of SHG signal energy output

Input power	KDP	5a	5c	5e
mJ/pulse	mV	mV	mV	mV
1.6	8.3	1.5	3.5	1.8

Among the tested compounds three azetidinone derivatives showed NLO property. Compounds, **5a** exhibited NLO property with SHG conversion efficiency 0.12 times that of potassium dihydrogen phosphate (KDP), compound **5c** exhibited NLO property with SHG conversion efficiency 0.42 times that of KDP, compound **5e** exhibited NLO property with SHG conversion efficiency 0.21 times that of KDP.

CONCLUSION

The optical SHG conversion efficiency of azetidinone derivatives has been investigated. The results demonstrated that the relative SHG conversion efficiency of the newly synthesized compounds indicate the suitability for NLO applications. Hence, there is plenty of scope for systematic study to evaluate the compounds for other pharmacological activities such as antiviral, anti inflammatory, analgesic activities. The substitutions could be varied to obtain more potent compounds. Moreover, an easy synthesis of these materials is an added advantage.

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