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Studies On Antiaminopyrine Substituted Triazine Moiety With Notable NLO Property

KEYWORDS: S-triazine, 4-aminoantipyrine, Fluorescence, SHG, Antimicrobial activity.

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ABSTRACT *An expedient method of novel triazine based compound containing triazine nucleus is synthesized. The structural features of the compound have been investigated by elemental analyses, $I^{R,\ 1H\ NMR}$ and Mass spectral studies. The synthesized compound can serve as potential photoactive materials as indicated from their characteristic fluorescence properties. The second harmonic generation (SHG) efficiency of the compound was found to be higher than that of urea and KDP. The in vitro antimicrobial activities of the compounds were tested against few microorganisms by well diffusion method and the result reveals that significant activity against Amikacin and Ketoconazole.*

1. Introduction

Recently the field of molecular nonlinear optics has attracted the attention of the researchers to search for nonlinear optical materials [1] and to improve the NLO efficiency of the known materials. In addition, molecular nonlinearlity deals with the essential issues such as charge transfer, hyper polarizabilities, conjugation and various applications in different fields including telecommunications [2], optical data storage and information processing [3], micro fabrication [4–6] and biological imaging [7, 8]. 1,3,5- triazines [9] have high electron mobility, thermal and photochemical stability, commonly it have been used as hole transporting materials or light emitting materials, since they have a wide range of applications in photovoltaic cells [10], organic light emitting diodes (OLED) [11] and polymer fields [12].

S-triazine derivatives have received considerable attention due to their potent biological activity such as anticancer [13], estrogen receptor modulators [14], antivirals [15], and antimalarials [16]. The compounds containing pyrazolone moiety have also been found to possess antitubercular and anti-inflammatory activities [17]. Hence, we aim to synthesis a new derivative of triazine with enhanced pharmacological activities and nonlinear properties. Here, we present the synthesis, spectral characterization, bioscreening, nonlinear optical property and fluorescence study of compound (Bis(4-Amino-1,2-dihydro-2,3-Dimethyl-1-Phenylpyrazol-5-ylidene)-6-phenyl-1,3,5-Triazine-2,4-diamine) (ADPT)

2. Experimental

All chemicals were obtained from Aldrich Chemical & Co. and used without purification which includes S-triazine and 4-Aminoantipyrine. All solvents including acetonitrile, dichloromethane (DCM), dimethylformamide (DMF), dimethylsulfoxide (DMSO), ethanol (EtOH) and ethyl acetate (EtOAC) were of analytical grade and procured from SD fine chemicals Limited (India) and used without purification. Fluorescence spectra were obtained on ELICO SL174 spectrofluorometer (Lady Doak College, Madurai) using Ethanol, and DMF as solvent. The IR spectra in KBr disc was recorded on a SHIMADZU FT-IR spectrophotometer at USIC, Madurai Kamaraj University, Madurai. ^{1}H NMR spectrum was recorded in DMSO using a Bruker DRX-300, 300MHz NMR spectrometer. EI mass was recorded at Madurai Kamaraj University, Madurai. The synthesized compound was screened for biological activity through the well-diffusion method. The SHG conversion efficiency of the compound was determined by the modified version of powder technique at IISC, Bangalore.

2.1. Synthesis of Bis (4-Amino-1,2-dihydro-2,3-Dimethyl-1-Phenylpyrazol-5-ylidene)-6-phenyl-1,3,5-Triazine-2,4-diamine (ADPT)

1g, (10 mmol) of 2,4-diamino-6-phenyl-1,3,5-triazine in ethanol was refluxed with 2.17g (20 mmol) of 4-aminoantipyrine for 6 h. The resulting solution was slowly evaporated and the yellow solid obtained was filtered and it is recrystallized from hot ethanol and dried in vacuum over anhydrous calcium chloride gave (ADPT) (80%) as the pure product (**Fig.1**).

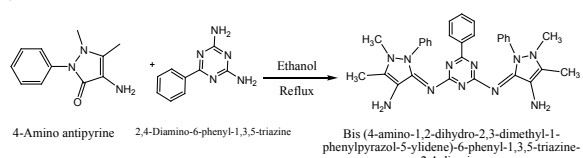

Fig.1. Synthesis of (ADPT)

2.2. Nonlinear Optical Properties

The SHG efficiency of compound was determined by the modified version of the powder technique developed by Kurtz and Perry [18]. The compound was ground into powder and packed between two transparent glass slides. An Nd:YAG laser beam of wavelength 1064nm was passed through the sample cell. The transmitted fundamental wave was absorbed by a copper(II)sulphate solution,

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which removes the incident 1064nm light and Filter BG-38 removing any residual 1064nm light. Interference filter band width is 4nm and central wavelength of 532 nm is used. Green light is finally detected by the photomultiplier tube and displayed on the oscilloscope. The second harmonic signal was detected by a photomultiplier tube and displayed on a storage oscilloscope. The efficiency of the sample was compared with microcrystalline powder of KDP and urea. The input energy used in this particular setup was 2.2mJ/pulse.

3. Results and Discussion

The synthesized compound (Bis(4-Amino-1,2-dihydro-2,3-Dimethyl-1-Phenylpyrazol-5- ylidene)-6-phenyl-1,3,5-Triazine-2,4-diamine)(ADPT) was obtained by the reaction of 4-Amino antipyrine with s-triazine. The compound (ADPT) is stable at room temperature and soluble in common organic solvents such as DMSO, DMF and acetonitrile. The compound is stable, non-hydroscopic, intensely colored and amorphous solid.

3.1. Elemental Analysis

The elemental analysis of the compound (ADPT) is in good agreement with the calculated ones. Calc (%) for ($C_{31}H_{31}N_{11}$): C, 66.77; H, 5.60; N, 27.63; Found (%): C, 66.79; H, 5.57; N, 27.66.

3.2. Spectral Studies

The IR spectrum of the compound (ADPT) was recorded using KBr pellets in the range 4000-400 Cm^{-1}. The compound exhibits intense bands at 1427 cm^{-1} and 1450 cm^{-1} which were characteristic of the ν (C-N) and ν (C=N) groups in S-triazine. A broad band at 3190 cm^{-1} is assigned to $\nu(NH_2)$ (**Fig.2**). The ^1H NMR spectrum of the compound shows a singlet at δ 2.82 ppm which corresponds to $-NCH_3$ protons and $-CCH_3$ protons appear as a singlet at δ 2.15 ppm and 6.27 ppm is assigned to $-NH_2$ protons of antipyrine. The aromatic protons appeared as multiplet in the range δ 7.23 – 7.68 ppm and the ortho protons of the phenyl ring appears as doublet at δ 8.3 ppm (**Fig.3**). The molecular ion peak for the compound (ADPT) was observed at 560 m/z which is in good agreement with the suggested molecular formula $C_{31}H_{31}N_{11}$ (**Fig.4**). The emission spectra of the compound (ADPT) were studied using two different solvents namely Ethanol and DMF. The compound exhibits fluorescence excitation maximum at λex = 299, 312 nm and an emission maximum at λem = 307, 318 nm respectively (**Fig.5**).

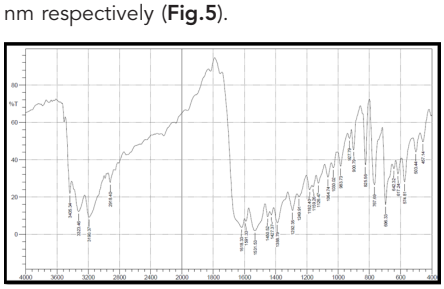


Fig.2. IR spectrum of ADPT

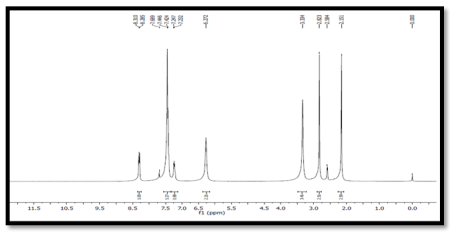


Fig.3. ^1H spectrum of ADPT

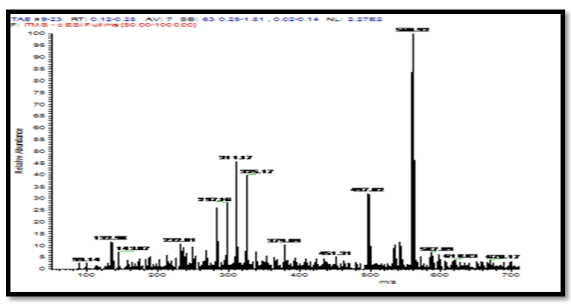
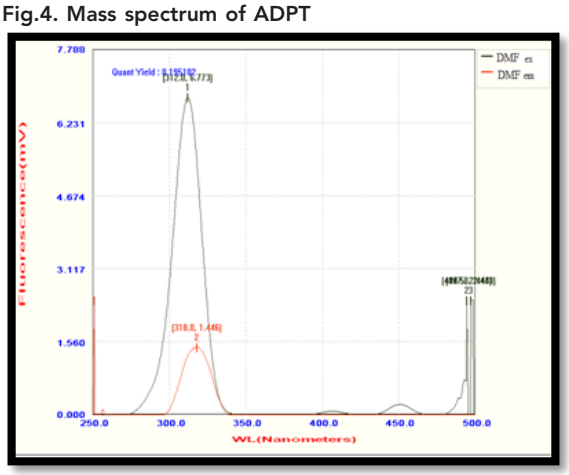


Fig.4. Mass spectrum of ADPT



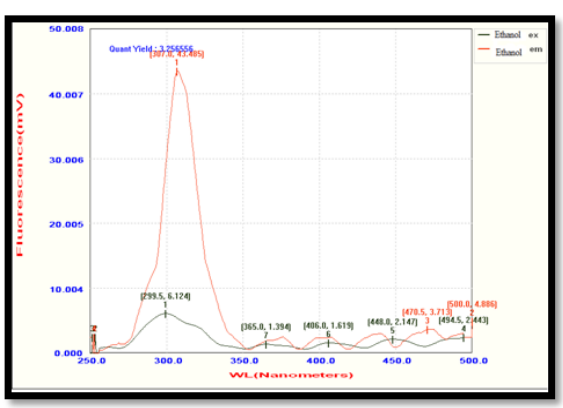


Fig.5.Flourosecnce spectrum of ADPT

3.3. Nonlinear optical property

The second harmonic generation (SHG) efficiency of the compound shows much higher efficiency than KDP and urea. This may be due to the presence of triazine and pyrazolone nucleus. In general, molecule with delocalized π-electron system can have large nonlinear polarizabilities [19] and it has been generally understood that the molecular non linearity can be enhanced by systems with strong donor and acceptor groups [20]. The second harmonic

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generation efficiency clearly reveals that the compound possesses equal activity than that of urea and 2 times more active than KDP.

3.4. Biological Activity

The newly synthesized compound (ADPT) was screened for antibacterial activity and antifungal activity by using well-diffusion method (**Table**). *Amikacin* and *Ketoconazole* were taken as the standard antibiotics and antifungi organisms. The tested compound showed a remarkable biological activity against different types of gram positive and gram negative bacteria (*Staphylococcus aureus, Bacillus subtilis, Escherichia coli* and *Pseudomonas aeruginosa,)* and fungi species (*Candida albicans* and *Aspergillus niger*). *In vitro* antifungal activity data of the compound against tested organisms displayed equal activity than the standards against *Aspergillus niger*. *In vitro* antibacterial activity data also reveals that the newly synthesized compound displayed significant activity in comparison to standards against *Staphylococcus aureus* and *Bacillus subtilis* (**Fig.6**).

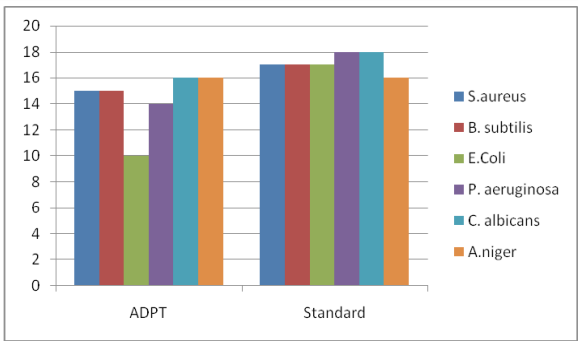

Fig.6. Antimicrobial activity of the compound (ADPT)

Table: Biological activity of the compound (ADPT) (zone of inhibition in mm).

Compound	S. *aureus*	B. *subtilis*	E. *coli*	*p. aeruginosa*	C. *albicans*	A. *niger*
$C_{31}H_{31}N_{11}$	15	15	10	14	16	16
standard	17	17	17	18	18	16

4. Conclusion

The newly synthesized compound (Bis (4-Amino-1,2-dihydro-2,3-Dimethyl-1-Phenylpyrazol-5- ylidene)-6-phenyl-1,3,5-Triazine-2,4-diamine) (ADPT) was obtained by the reaction of 4-aminoantipyrine with s-triazine. The structure of the compound was assigned by using elemental, mass and ^{1}HNMR spectral details. The compound exhibits appreciable nonlinear property in comparison with KDP and urea. Hence, the compound can be utilized for further NLO investigations. The synthesized compound (Bis (4-Amino-1,2-dihydro-2,3-Dimethyl-1-Phenylpyrazol-5-ylidene)-6-phenyl-1,3,5-Triazine-2,4-diamine) (ADPT) is fluorescent in nature. The compound was potentially active towards all microbial strains.

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