Synthesis of 2-Methoxy 5-nitro9,10-anthraquinone and study of photophysical properties

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ABSTRACT

Literature survey reveal that a good number of Anthracene and substituted Anthracene are potential lasing organic compounds. As per mit suo meada[66] 9,10-dimethyl and 9,10-diphenyl Anthracenes exhibit lasing properties, around 435-450 nm (ethanol). In continuation of our studies in this lab, our objective is to synthesize new lasing organic dyes, in particular, new Anthracene derivatives and study their photo physical properties, besides the lasing characterization.

2,6-disubstituted or 2,5 – di-substituted Anthracenes are our choice. Hence, it is proposed to synthesize 2-Methoxy, 5-nitro, 9, 10-Anthraquinone and to examine whether these type of molecules also exhibit lasing properties. Initially it is preferred to study the photo physical properties for better understanding of the lasing phenomena. The synthetic route for the synthesis of 2-Methoxy, 5-nitro, 9,10-Anthraquinone is described below in (Scheme -1).

Key words: Photophysical properties,

INTRODUCTION

The word 'LASER' is an acronym derived from light amplification by the stimulated emission of radiation. If the light concerned happens to be in the microwave region then the word 'MASER' is used. Lasers entered the scene at a time when several hundreds of laser active materials had already been found. Yet, they were not just another addition to the already long list of lasers. Lasers are attractive in several other respects. These can be used in the solid, liquid, or gas phases and their concentration, and hence their absorption and gain, is readily controlled.

Every speculations about the use of organic compounds produced correct expectations of the role of vibronic levels of electronically excited molecules. But, the first experimental study that might have led to the realization of an organic laser. Every dye laser is operated by optical pumping, except for one that is operated by electron beam pumping (278). There are two types of light sources used for optical pumping. That is coherent and incoherent sources.

In dye lasers, the dye is mixed or doped in either of the following host materials. (1) an organic or inorganic liquid solvent. (2) A plastic host or organic crystal (3) a liquid crystal matrix. And (4) buffer gas or vacuum (in vapourised phase). The ordinal form is the liquid phase. The solvent and its concentration are important factors in determining the lasing wavelength and efficiency. Sometimes, two solvents are mixed together. The viscosity is also an important factor.

The dye laser may be viewed as a 'four-level' system. In this, the mass probable excitation proceed to populate upper vibrational level in S_1, a vibrational relaxation to the 'zeroeth' level in S_1 follows.

1. Surface active agents to prevent dimerisation of dye molecules
2. Mixing of lasing compounds. When excited energy is successfully transferred from donor molecules, to acceptor molecules, the later are sensitized.
3. To control the pH value in the solution, a small amount of NaOH or Acid is added.

Lasing action principle and practice:

Lasers are sources of radiation with unique properties. They operate by the process of induced emission which is importance than spontaneous emission. If a photon is absorbed by an atom in the lower state of energy so and thereby goes to a higher state of energy S_1, it can reverse to the lower state, spontaneously by emitting a photon with the energy (S_1-S_0) at the frequency n = $(S_1 − S_0)$ / h where h is planks constant. This is the spontaneous emission (Fluorescence) or without emission (internal conversion) as well as to a tripler state (inter system crossing). If, however the atom happens to be in state S_1, when the field of frequency $v = S_1-S_0$ / h is first applied, it will make a down ward transition to state. So, emitting in the process a photon of energy *hv*. This is induced transition. The induced transition differs from the spontaneous one in the fact that the induced rate is proportional to the intensity of the electro magnetic field. Whereas the spontaneous rate is independent of it. Also, the induced transition rate for the transitions. S_0 to S_1 and S_1 to S_0 are equal where as the spontaneous transition rate for the transition S_0 to S_1 (in which energy of the atom increases) is zero emission occurs to repopulate an upper level of the ground state (S_0).

Laser light differs from ordinary thermal radiation in respect of high direction, high spectral brightness and a high degree of special and temporal coherence. Spectral purity of mono-chromacity of the laser radiation is an important feature of coherent sources and temporal coherence is a consequence of it. For most laser applications the amplifying medium is enclosed. In an optical cavity for feed back and mode selection i.e. it is part of laser oscillator. Only light from coherent sources will produce useful signals at the output.

Applications:

· Industry
    1.Laser hardening 2. Laser welding
    3. Laser drilling 4. Laser cutting
    5. Material processing 6. Marking.

· Medicine Certain applications, such as the attempted destruction of cancers and tumors with laser light. The removal of dental caries, or the treatment of fractured bones. A lightly focused intense laser bean can be used for bloodless and sterile surgery.
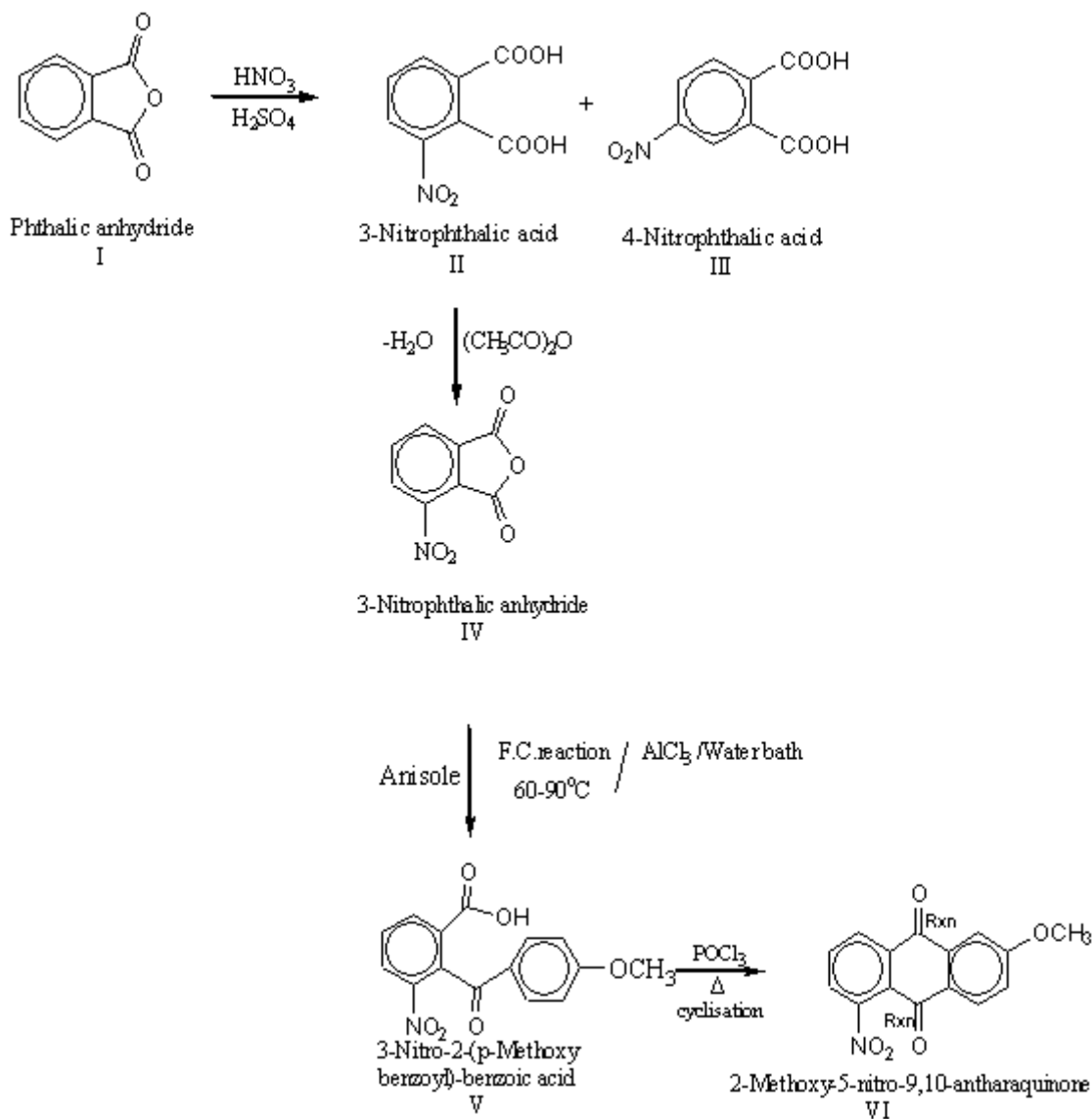
Intense laser pulses can remove tattooing, without pain and without the scarring encountered in surgical removal. Laser irradiation has also been helpful in the treatment of certain disfiguring skin pigmentation. And it is also used for eye surgery by photo coagulation

· Distance measurement
· Biology
· Chemistry
(1). Photochemistry and isotope separation
(2). Trace analysis, pollution detection
· Holography
· Warfare
· Under water studies
· Spectroscopy
· Communication

Hence it is proposed to synthesize 2,5 substituted Anthraquinone VI molecule and then to study their photophysical properties. The synthetic scheme is presented in Scheme-I.

Step I: Synthesis of 3-Nitro Phthalic acid (II)
Procedure: Equip a 500ml, three-necked round bottomed flask, supported on a water bath, with a dropping funnel, a thermometer and a stirrer supported in a central (open) neck connected by means of a flexible drive to a stirrer motor. The later should not be sited near the open neck, since the nitrous fumes evolved in the subsequent reaction may otherwise cause damage. Place 100gm (0.675ml) of technical phthalic anhydride and 100ml of concentrated sulphuric acid in the flask and heat it until the temperature of the mixture rises to 80ºC. Remove the water bath, and add a mixture of 42 ml of fuming nitric acid (d 1.5) and 30 ml of concentrated sulphuric acid slowly from the dropping

Scheme 1

funnel at such a rate as to maintain the temperature of the stirred mixture at 100-110°C (about 1 hour). Then add 180 ml of concentrated nitric acid (d 1.42) as rapidly as possible, without causing the temperature to rise above 110°C. Heat the mixture on the water bath, with stirring, for 2 hours. Flow the reaction mixture to stand over night and the pour it into 300 ml of water contained in a 2 – liter beaker. Cool and filter the mixture of 3- and 4- Nitrophthalic acids through a sintered glass funnel. Return the wet cake of acids to the rinsed out beaker

and stir it thoroughly with 40 ml of water, which dissolves a large amount of the 4-Nitrophthalic acid. Filter again at the pump and dissolve the solid in 40-60 ml of boiling water. Filter the hot solution and stir until crystallization commences and then leave overnight until crystallization is complete. Filter again under suction and dry on filter paper.

Yield   :   20gms
MP   :   216°C
HPLC   :   97.91% pure
IR   :   1710 cm^{-1}, 1610 cm^{-1}.;

1365cm^{-1}(N-O str)

NMR   :   δ 7.4 -δ 7.5; δ 11.5 (acid protons)

Step II: Synthesis of 3-Nitro Phthalic anhydride-IV

Procedure: In a 100ml round bottomed flask fitted with a reflux condenser, place 21 gm. (0.1ml) of 3-nitrophthalic acid and 20gm (18.5 ml, 0.2 ml) of redistilled acetic anhydride. Heat the mixture to gentle boiling until a clear solution is obtained, and then for about 10 minutes longer, pour the hot mixture into a large porcelain dish and allow to cool. Grind the crystalline mass thoroughly in a mortar and filter at the pump through a sintered glass funnel. Return the crystals to the mortor, grind them with 15ml of sodium dried ether and filter. Again return the crystals to the mortor and wash once more with 15ml of dry, alcohol free ether. Dry in air for a short time, and then to constant weight at 100°C.

Yield   :   16gms
MP   :   164°C
HPLC   :   98.5% pure
IR   :   1785 cm^{-1}, (anhydride carbonyl);
                    1620 (aromatic C=C)
NMR   :   δ 7.4 - δ 7.2; (aromatic protons)

Step III: Synthesis of 3-Nitro, 2-(p-methoxy benzoyl), Benzoic acid(V)

Procedure: Place a mixture of 1.0gm of the methoxy benzene, 20 ml of dry dichloromethane, 2.5gm of powdered anhydrous AlCl$_3$, and 1.2gm of pure 3-nitrophthalic anhydride in a 25-50ml round bottomed flask fitted with a reflux condenser. Heat on a water both for 30 minutes. (or until no more HCl fumes are evolved). Cool in ice and 10 ml of concentrated HCl cautiously and with constant shaking. When the reaction has subsided, add 20ml of water and shake vigorously. (All the solid material should pass into solution). Transfer the two-phase system to a separating funnel, add 25ml of ether and shake. Discard the lower aqueous phase. Wash the ethereal layer with 25ml of 2.5m HCl to ensure removal of any aluminium salts present. Shake the ethereal solution cautiously with 25ml of ethyl acetate solution and run the aqueous phase slowly into 30 ml of water. Collect the aroyl benzoic acid by suction filtration, wash it with 25-30ml of water and recrystallise it from dilute ethanol or from acetic acid. The derivatives prepared from benzene and toluene crystallize with water of crystallization, the latter is removed by drying at 100°C.

Yield   :   0.69gms
MP   :   172°C
HPLC   :   97.55% pure
IR   :   1710 cm^{-1} (C=O); 1600 (C=C);
                    1105 (O-C Str)
NMR   :   δ 3.6 (3H; methoxy protons),
                    δ 7.3 - δ 7.6;
                    (aromatic protons), δ 11.5
                    (acid protons)

Step IV: Synthesis of 2-Methoxy, 5-nitro-9,10-Anthraquinone (VI)

Procedure: In a typical experiment the compound V (0.01 mole) was mixed with a slight excess of (0.015 mole) of pyrophosphoric chloride or a large excess of phosphorous oxy chloride (0.05 mole). The mixture was warmed for a certain period of time (30 min) [for the active substrates to several hours for the less active ones] the reaction mixture was quenched with cold water or ice. And the ketone was extracted with EtoAc. The organic layer was washed with an ethyl acetate and dried over MgSO$_4$. Evaporation of the organic solvent afforded the crystalised product. The products were recrystallised from ethanol

Yield   :   200mg
MP   :   182°C
HPLC   :   98.9% pure
IR   :   1710 cm^{-1}; 1620 (C=C); 1120
                    (O-C Str)
NMR   :   δ 3.6 (3H; methoxy protons),
                    δ 7.2 - δ 7.6; (aromatic protons),
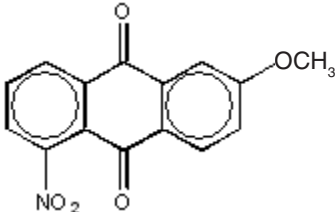
Study of Photophysical Properties

In continuation of the above programme, the newly synthesized compound, 2-Methoxy, 5-nitro, 9,10-Anthraquinone (VI) is examined for its photophysical properties Viz Fluorescence emission spectrum (Fig-3.1) as excitation spectrum (Fig-3.2). Further the stokes shift (Table-III) is also calculated to understand the lasing characteristics before the molecule is studied for laser properties.

Fluorescence Spectrum (Emission)

The fluorescence emission spectrum is recorded on spectrofluorimeter (Shimadzu instrument) and the data is recorded below in Table 1.

Table 1:

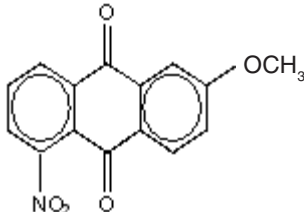| S.No	Compound	Solvent Used	Emission Max λ_f nm
1.	2-Methoxy, 5-nitro, 9,10-Anthraquinone	Ethanol	460nm

Fluorescence Spectrum (Excitation):

The excitation spectrum is also recorded in ethanol and the data is presented in Table-II. Calculation of Stokes shift:

In order to understand the lasing phenomena, it is always advisable to calculate the stokes shift. Hence to the newly synthesized compound, the strokes shift is calculated and presented below:

Table 2:

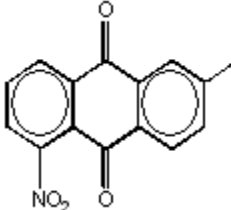| S.No	Compound	Solvent Used	Excitation Max λ_a nm
1.	2-Methoxy, 5-nitro, 9,10-Anthraquinone	Ethanol	410nm

Calculation of Stokes shift

In order to understand the lasing phenomena, it is always advisable to calculate the stokes shift. Hence to the newly synthesized compound, the strokes shift is calculated and presented below:

Table 3:

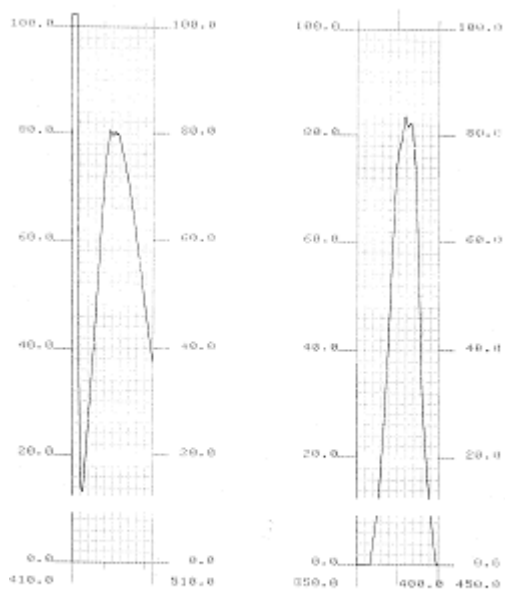| Stokes shift of the compound 2-Methoxy, 5-nitro, 9,10-Anthraquinone	$\lambda_f - \lambda_a = 460 - 410 = 50nm$

RESULTS AND CONCLUSIONS

It is proposed to synthesize new molecules Viz 5-Nitro,2-methoxy Anthraquinone (by IR, NMR etc) and the structural elucidation and chemical analysis is carried out to establish the structure of the Target molecule (compound-VI). Further the Photophysical properties are also investigated.

Fluorescence emission and excitation spectra were experimented besides stokes shift to understand the lasing phenomena. From the data, it is evident that the new molecule (VI) may exhibit the lasing maxima around 500nm; which falls under blue-green region. These studies are new and more work is to be carried out to confirm the above data.

Fig. 3.1.

Spectrum of fluorescence emission of
2-Methoxy,5-nitro,9,10-Anthraquinone

Fig. 3.2.

Spectrum of fluorescence excitation of
2-Methoxy, 5-nitro,9,10-Anthraquinone

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