Synthesis of 2-chloro 5-nitro 9,10-anthraquinone and the study of photophysical properties

Y.L.N. MURTHY[1], CH.V.V. SATYANARAYANA MURTHY[2],
K. SRIHARI VARMA[2] and B.VIJAYA KUMARI[2]

Departmnet of Organic Chemistry, Andhra University, Visakhapatnam - 530 003 (India).
P.G. Departemnt of Chemistry, Ideal College of Arts and Sciences,
Vidyutnagar, Kakinada - 533 003 (India).

ABSTRACT

Literature survey revealed that a good number of anthracene and substituted anthracences are potential lasing organic compounds. As per Mitsuo Maeda 9,10 dimethyl and 9,10 diphenyl anthracenes exhibit lasing properties around, 435-450nm. In continuation of our studies[27] it was proposed to synthesize new lasing organic dyes in particular, new anthracene derivatives and study their photophysical properties besides the lasing characteristics. Search of literature indicate that 9,10 disubstituted anthracenes are well synthesized and reported. Hence we propose to synthesize 2,6 disubstituted anthracenes and 2,5 disubstituted anthracenes. In the first instance, it is proposed to synthesize 2,5 disubstituted anthraquinones which on reduction yield the target molecules (TM). 2,6-disubstituted or 2,5-disubstituted anthrancenes are our choice. Hence it is proposed to synthesize 2-Chloro, 5-nitro, 9,10-anthraquinone and to examine whether these type of molecules also exhibit lasing properties. Initially it is advisable to study the photophysical properties for better understanding of the lasing phenomena. The synthetic route for the sysnthesis of 2-Chloro, 5-nitro; 9-10-Anthraquinone is described below in scheme 1.

Key words: Synthesis, Anthraquinone derivatives, 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.

Lasing action principle and practice

Lasers are sources of radiation with unique properties. They operate by the process of induced emission which is of prime importance than spontaneous emission. If a photon is absorbed by an atom in the lower state of energy s_o and thereby goes to a higher state of energy s_1, it can revert to the lower state, spontaneously by emitting a photon with the energy (s_1-s_o) at the frequency n = (s_1-s_o) / h where h is Planck's constant. This is the spontaneous emission (fluorescence) or without emission (internal conversion) as well as to a triplet state (intersystem crossing). If however the atom happens to be in state s_1 and when the field of frequency n = s_1-s_o/h is first applied, it will make a downward transition emitting in the process a photon of energy hn. This is called induced transition. The induced transition differs from the spontaneous one in the fact that the induced rate is proportional to the intensity of the electromagnetic field where as in the spontaneous rate for the transitions s_o to s_1 and s_1 to s_o are equal whereas the spontaneous transition rate for the transition s_o to s_1 (in which energy of the atom increases) is zero.

For induced emission from the upper energy level s_1 to the lower energy level. For induced emission from the upper energy level s_1 to the lower energy level s_o to dominate induced absorption there must be a population inversion between the two levels, i.e., $s_1 > s_o$. The population inversion requires an input of energy. The process by which such an inversion is brought about is known as pumping. A system in which population inversion has been created is called an active medium or lasing medium.

The dye laser may be viewed as a 'four – level' system, in that the most probable excitations proceed to populate upper vibrational levels in **s_1**, a vibrational relaxation to the 'zeroth' level in **s_1** follows, and emission occurs to repopulate an upper vibrational level of the ground state (s_o).

Laser light differs from ordinary thermal radiation in respect of high directionality, high spectral brightness and a high degree of spatial and temporal coherence. Another property of laser radiation which gives if an advantage over the thermal radiation is its ability to be focused in very small dimensions.

Spectral purity or monochromaticity of the laser radiation is a characteristic feature of coherent sources and temporal coherence is a consequence of it.

Different lasing materials

Depending upon the active medium or lasing medium the laser system can be classified into the solid[3], liquid[4], gas[5] and semiconductor[6] lasers.

Solid lasers may be cr^{+3}: Al_2O_3 (ruby)[7], Nd^{3+}: YAG[8] (neodymium: yttrium aluminium garnet $Y_3Al_5O_{12}$), Nd Glass[9], fibre glass lasers. Liquid lasers may be the rare earth ions in liquid solvents constitute the inorganic liquid laser. Gas lasers may be Atomic (He Ne laser[12]), ionic (noble gas ion laser like Ar, Kr laser) molecular (co_2 laser[13], N_2 laber[14]) and the excimer lasers[15].

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 1.

EXPERIMENTAL

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 the 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 (0.675 mol) of technical Phthalic anhydride and 100ml of concentrated sulphuric acid in the flask and heat it until the temperature of the mixture rises to 80^0C. Remove the water bath and add a mixture of 42ml of fuming nitric acid (d1.5) and 30ml of concentrated sulphuric acid slowly from the dropping funnel at such a rate as to maintain the temperature of the stirred mixture at $100\text{-}110^0C$ (about 1 hour). Then add 180ml of concentrated nitric acid (d 1.42) as rapidly as possible, without causing the temperature to rise above 110^0C. Heat the mixture on the water bath, with stirring, for 2 hours. Flow the reaction mixture to stand overnight and then pour it into 300ml of water contained in a 2 litre 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 40ml of water, which dissolves a large amount of the 4-Nitrophthalic acid. Filter again at the pump and dissolve the solid in 40-60ml of boiling water; fitter the hot solution and stir until crystallization commences and then leave overnight until crystallization is complete. Filter again with suction and dry upon filter paper.

Yield : 20gms

m.p. : 216^0C

HPLC : 99.55% pure

IR : 1710 cm^{-1} (C=O) , 1610 cm^{-1} (C=C) ; 136 cm^{-1} (N- O Str)

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

TLC : Single: R_f. 0.45

STEP – II: Synthesis of 3-Nitro Phthalic Anhydride-IV
Procedure

In a 100ml round-bottomed flask fitted with a reflux condenser, place 21 gm (0.1mol) 0f 3-nitrophthalic acid and 20gm (18.5ml,0.2ml) of

redistilled acetic anhydride, heat the mixture to gentle boiling until a clear solution is obtained, and then for about 10minutes longer. Pour the host 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 mortar, grind them with 15ml of sodium-dried ether and filter. Again return the crystals to the mortar and wash once more with 15ml of sodium-dried ether and filter.   Again return the crystals to the mortar and wash once more with 15ml of dry, alcohol free ether. Dry in air for a short time, and then to constant weight at 100^0C.

Yield   :   17gms
m.p.   : 163^0C
HPLC   :   88% pure
IR   : $1785cm^{-1}$ (anhydride) (C=O); 1365 cm^{-1} (N-O Str)
NMR   : δ 7.30, 7.15 (3H)
TLC   :   Single, $R_f = 0.5$

Step-III Synthesis of 3-Nitro, 2-(p-chloro benzoyl), benzoic acid (V)
Procedure

Place a mixture of 1.0gm of the chlorobenzene, 10ml of dry dichloromethane, 2.5gm, 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 bath for 30 minutes (or until no more HCl fumes are evolved). Cool in ice and 10ml 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 seperatory funnel, add 25 ml of ether and shake. Discard the lower aqueous phase, wash the ethereal layer with 25ml of 2.5 M HCl to ensure removal of any aluminium salts present. Shake the ethereal solution cautiously with 25ml of sodium carbonate solution, and run the aqueous phase slowly into 30ml of hydrochloric acid collect the 3-Nitro, 2-(P-Chloro benzoyl), Benzoic acid by suction filtration, wash it with 25-50ml of water and recrystalise 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 100^0C.

Yield   :   1.2 gms
m.p.   : 180^0 C
HPLC   :   99.25%
IR   : $1705 cm^{-1}$ (C= O) ; $1610cm^{-1}$ (N-O Str)
NMR   : δ 11.25 (1H, COOH Protons), δ 7.35-7.70(7H, aromatic protons)
TLC   :   Single, $R_f = 0.5$

Step-IV Synthesis of 2-Chloro, 5-nitro anthraquinone (VI)
Procedure

In a typical experiment the compound (V) (0.01 mole) was mixed with a slight excess of
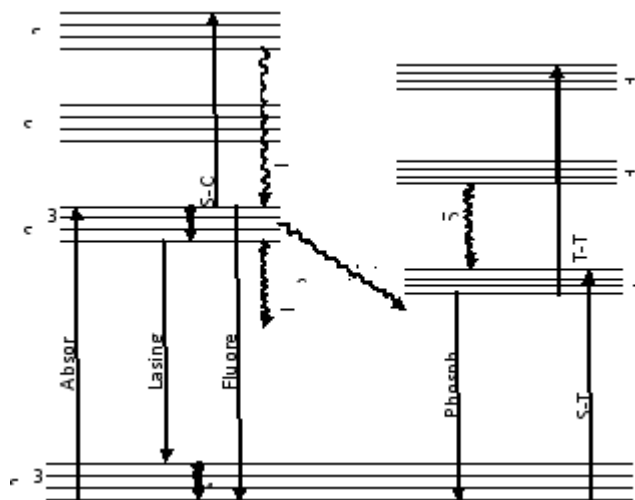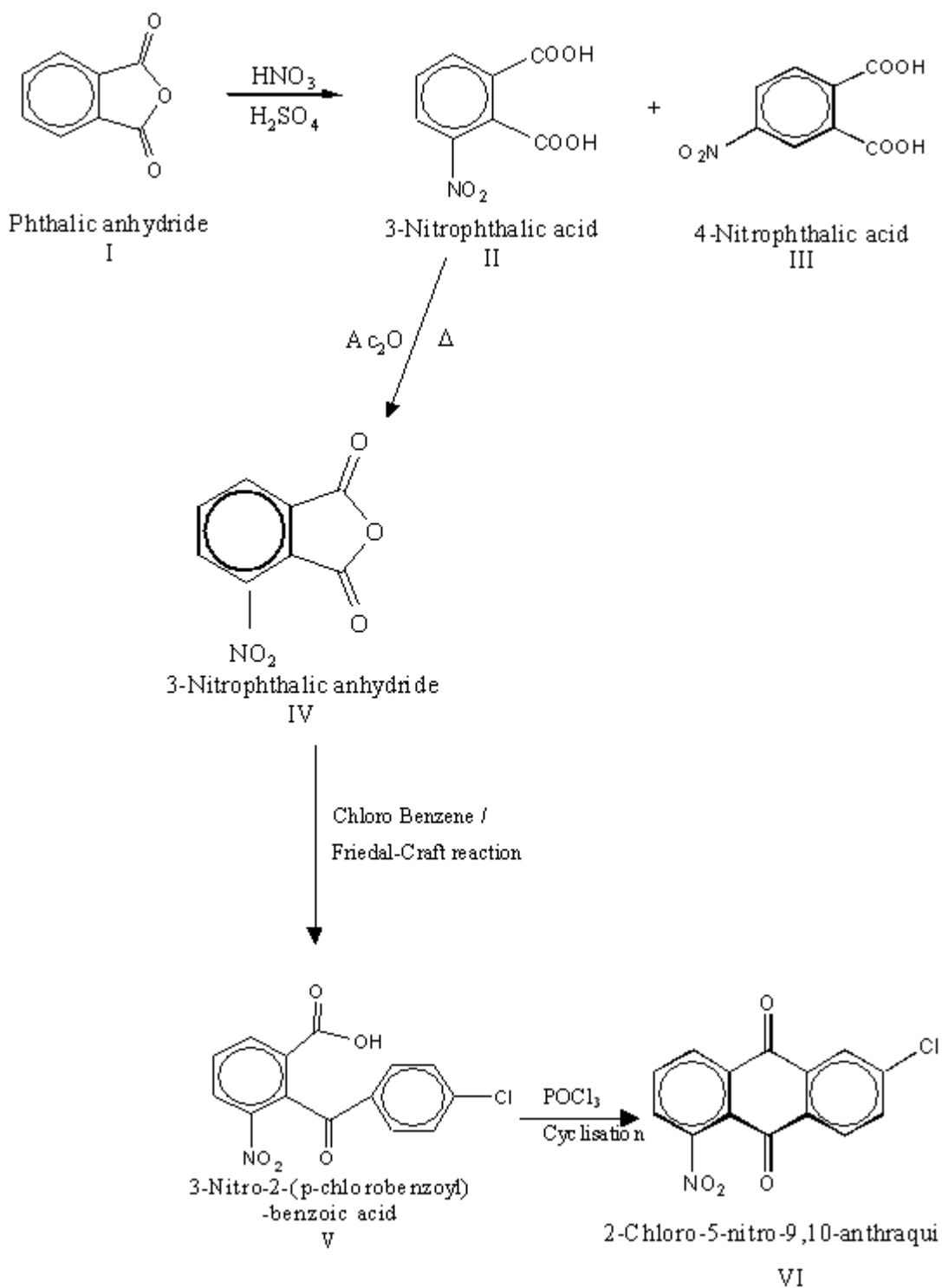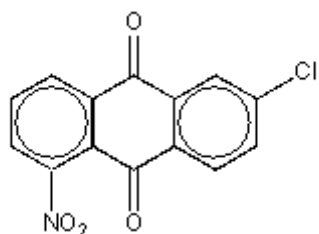

**Fig. 1: Jablonski diagram for excitation and emission**

Phthalic anhydride
I

3-Nitrophthalic acid
II

4-Nitrophthalic acid
III

3-Nitrophthalic anhydride
IV

3-Nitro-2-(p-chlorobenzoyl)
-benzoic acid
V

2-Chloro-5-nitro-9,10-anthraqui
VI

Scheme 1

Table 1

S.No	Compound	Solvent Used	Emission Max λ_f nm
1.	2-Chloro, 5-nitro, 9,10-Anthraquinone	Ethanol	435 nm

Table 2

| S.No	Compound	Solvent Used	Emission Max λ_f nm
1.	2-Chloro, 5-nitro, 9,10-Anthraquinone	Ethanol	405 nm
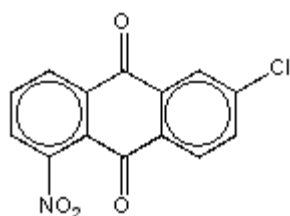
Table 3

Stokes shift of the compound 2-Chloro, 5-nitro, 9,10-Anthraquinone   = λ_f-λ_a = 435 -405 = 30nm
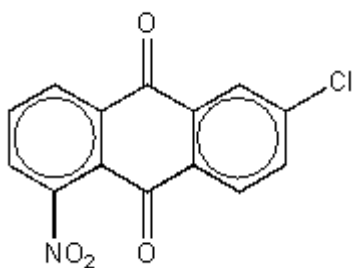
phosphorus oxychloride (0.05 mole). The mixture was warmed for a certain period of time, (30min) (for the active substrates to several hours for the less active ones). The reaction mixture was quenched with cold water or ice and the ketone was extracted with ether or $CHCl_3$. The organic layer was washed with a dil $NaHCO_3$ solution and dried over $MgSO_4$. Evaporation of the organic solvent
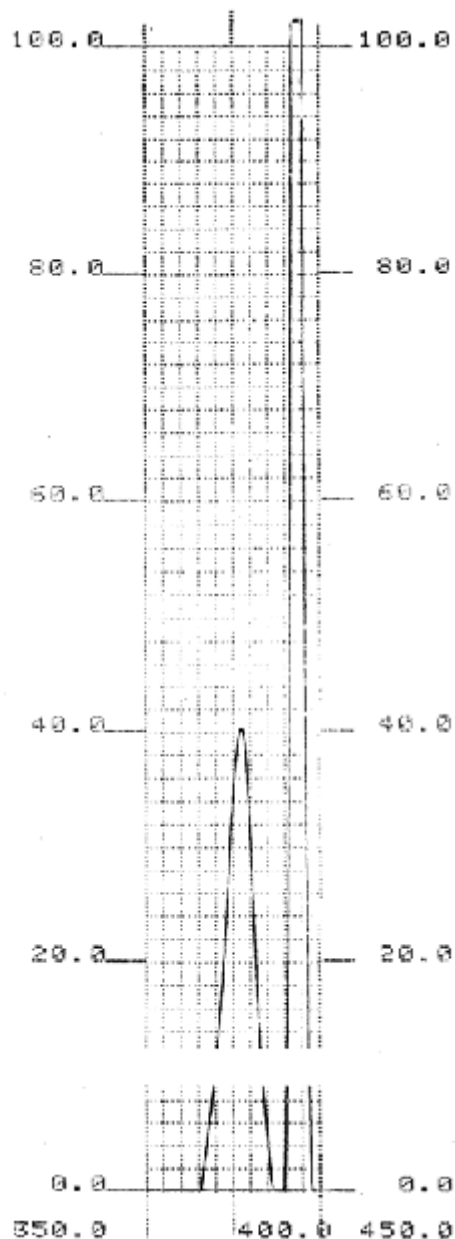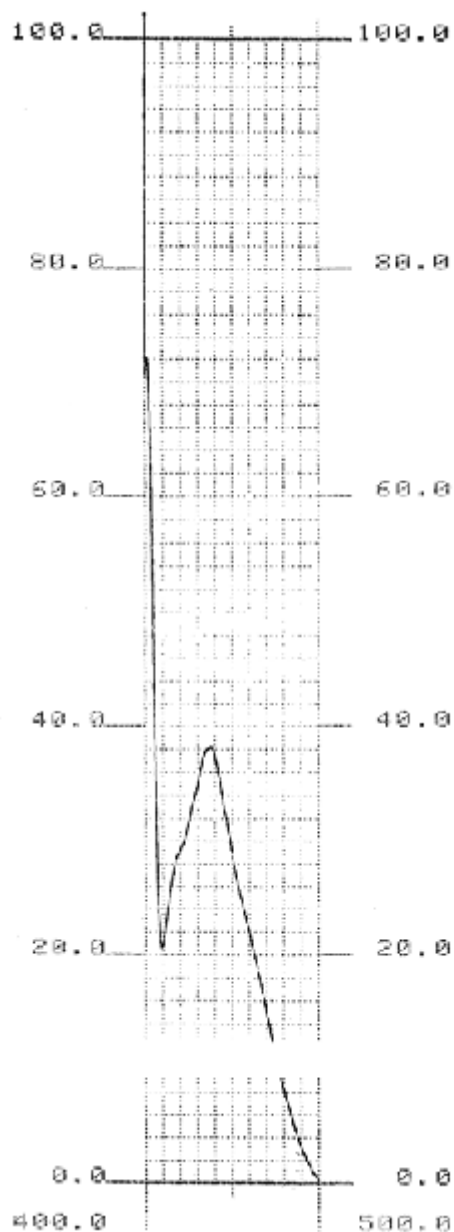
⊕ **Shimadzu corporation Chart 200-91527**

Fig. 3.1: Spectrum of fluorescence emission of 2-Chloro, 5-nitro, 9,10-antraquinone

Fig. 3.1: Spectrum of fluorescence excitation of 2-Chloro, 5-nitro, 9,10-antraquinone

afforded the cyclised product. The products were ether recrystallised or purified from ethanol.

Yield	:	150 mg
m.p.	:	184⁰ c
HPLC	:	95.55% pure
IR	:	1660cm⁻¹ (C=O), 690cm⁻¹ (C-Cl)
NMR	:	δ 7.7 – 7.85(3H) δ 7.3-7.5 (3H)\
TLC	:	Single, R$_f$ = 0.62

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Study of photophysical properties

In continuation of the above programme, the newly synthesized compound, 2-Chloro, 5-nitro, 9,10-Anthraquinone (VI), is examined for its photophysical properties viz Fluorescence emission spectrum (Fig. 3.1) and excitation spectrum (Fig. 3.2), further the stokes shift (Table 3) is also calculated to understand the lasing characteristics before the molecule is studied for laser properties.

Fluorescence Spectrum (Emission Max)

The fluorescence emission spectrum is recorded on spectro fluorimeter (shimadzu instrument) and the data is recorded below in Table 1.

Fluorescence spectrum (Excitation Max)

Similarly the excitation spectrum is also recorded in ethanol and the data is presented in Table 2.

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 2-Chloro, 5-nitro, 9,10-anthraquinone (VI) the strokes shift is calculated and presented below

RESULTS AND DISCUSSION

The proposed objective of synthesis of new molecule is achieved and the new compound is characterized by the advanced spectroscopic data. Further the molecule is compared with its isomer and the physical and spectral properties are recorded and observed as different. Further the compound 2- Chloro, 5-nitro, 9,10-Anthraquinone (VI) is studied for its emission maxima, absorption maxima and stokes shift. The data confirms that the molecule will exhibit (or may exhibit) lasing maxima around 470-500nm and Nd-YAG dye Laser may be useful in this study. Studies are in progress at Laser Technology Division, C.A.T., Indore.

This is the first report of the synthesis of such a molecule and the objective is new.

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