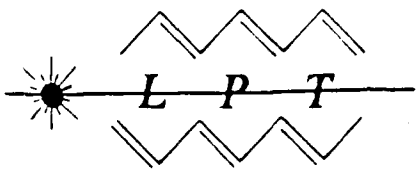


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LASER PHOTONICS TECHNOLOGY, INC.

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CHEMICAL PROCESSING OF NOVEL MULTIFUNCTIONAL MATERIALS  
FOR SENSOR PROTECTION AGAINST LASER THREATS

FINAL REPORT

MAY 1991

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**13. ABSTRACT (Maximum 200 words)**

There is an immediate need for the development of materials that could function to protect human vision and light sensitive equipment from laser based weapons. The goal of the just concluded research was to synthesize a compound that would incorporate a nonlinear two photon absorbing functional group adjacent to a photoreactive moiety. This innovative approach would lead to broad band high optical transparency at lower power levels and efficient and fast attenuation at higher power levels. The use of organic compounds in this application ensures that the molecular structure could be further optimized by careful adjustment of the molecular structure. The synthesized compound, anthracene leuconitrile, was found to be photochemically unstable and took an inappropriately long time for the reconversion from the absorbing to the transmitting form.

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## 1. EXECUTIVE SUMMARY

There is an immediate need for the development of materials that could function to protect human vision and light sensitive equipment from laser based weapons. The goal of the just concluded research was to synthesize a compound that would incorporate a nonlinear two photon absorbing functional group adjacent to a photoreactive moiety. This innovative approach would lead to broad band high optical transparency at lower power levels and efficient and fast attenuation at higher power levels. The use of organic compounds in this application ensures that the molecular structure could be further optimized by careful adjustment of the molecular structure.

The chief objective was to synthesize and evaluate a triarylmethane leuconitrile (TAML) which as a class of chemicals has shown to be photoionized with high efficiency yielding a highly colored dye cation. Absorption of light by these molecules is normally considered to be localized on the single aromatic rings; the entire absorption of the molecule is, to a first approximation, the sum of the component chromophore groups. The introduction of a moiety having a large two-photon absorption cross-section in place of a third aromatic system is expected to extend the frequency range throughout the visible spectral range.

The synthesis of 9-anthracene-bis(dimethylaminophenyl)methane leuconitrile can be done in one of two ways which were to shown to have very different yields. The first method is detailed in Approach I and the more successful method is described in Approach II. A number of synthetic steps proved to be difficult to optimize; carefully monitoring the more studied reactions with malachite green carbinol were used to find the optimal conditions.

The final compound was found to be photochemically unstable. The

compound was converted to the dye form upon addition to polar solvents, drying the compound and exposure to sunlight. In addition, the reversion to the native compound from the dye was inappropriately slow and, to be effective, had to be heated in the dark. Intensity dependent absorption evaluated with a number of laser systems (variable intensities and frequencies) proved insufficient for the proposed applications. Laser Photonics Technology, Inc. has decided not to submit a Phase II proposal. While the approach is fundamentally sound, subsequent steps to achieve the proposed goals are not straight forward. A Phase II effort at this time would be not be sufficiently directed and could not guarantee reasonable success.

### 3. SYNTHESIS OF LEUCO NITRILES.

The objective of the Phase I work was to demonstrate the feasibility of a new approach in designing a triarylmethane leuconitriles (TAMs) which promise to have an advantage over existing materials, organic or inorganic, as broad band optical attenuator and power limiter. The design of such material was based upon the incorporation of a nonlinear two-photon absorbing group adjacent to a photoreactive group.

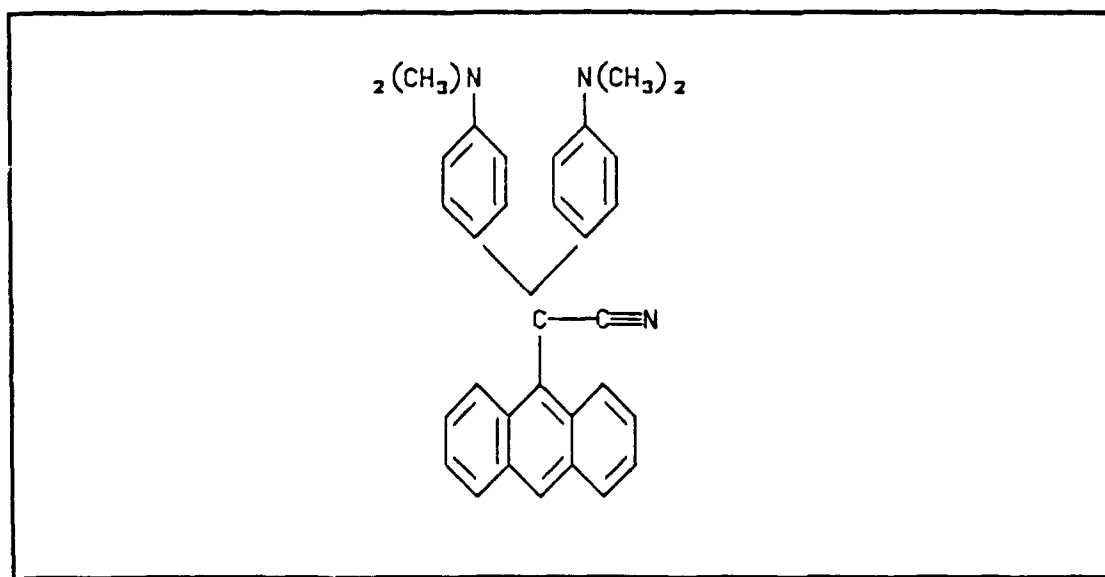


Figure 1. Anthracene Leuconitrile

[ 9-anthracene-bis(dimethylaminophenyl)methane leuconitrile ]

Based on extensive studies performed during recent years [1-3], the TAMs have been known to undergo UV photochemical ionization with a high quantum efficiency in polar solvents, regardless of light intensity and temperature. This process leads to the formation of highly absorbing dye in the visible frequency (TAMs are transparent in the visible). However, the photoionization frequency range can be extended towards the visible range if the TAM is composed of the group possessing a large two-photon absorption cross-section.

The main objective of the proposed work was the synthesis of a TAML by condensing p-bromo N,N-dimethylaniline with appropriately substituted aromatic compound. Anthracene was chosen as one of the ligands since it exhibits a strong two-photon absorption at ca. 600nm. The structure of anthracene leuconitrile is shown in Figure 1.

### 3.1. SYNTHESIS: APPROACH I (GENERAL)

Synthesis of triarylmethane leuconitrile has been well known for structures involving phenyl or substituted phenyl groups as aryl substituents. The synthetic route in Approach I followed these methods and consisted of four major steps as shown schematically below.

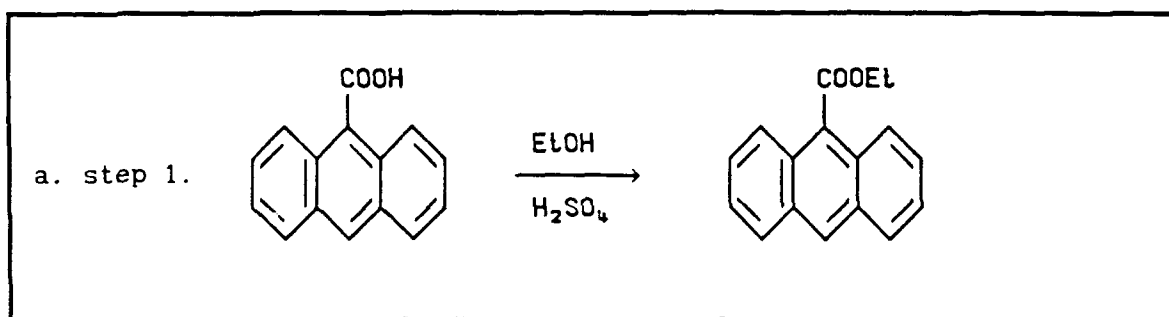


Figure 2. Reaction 1: esterification of 9-anthracic acid

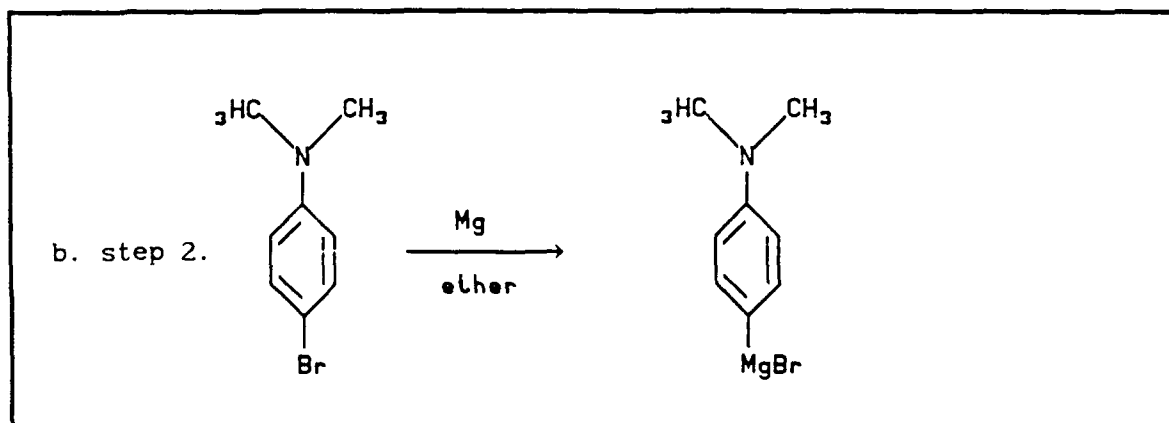


Figure 3. Reaction 2: Grignard reaction



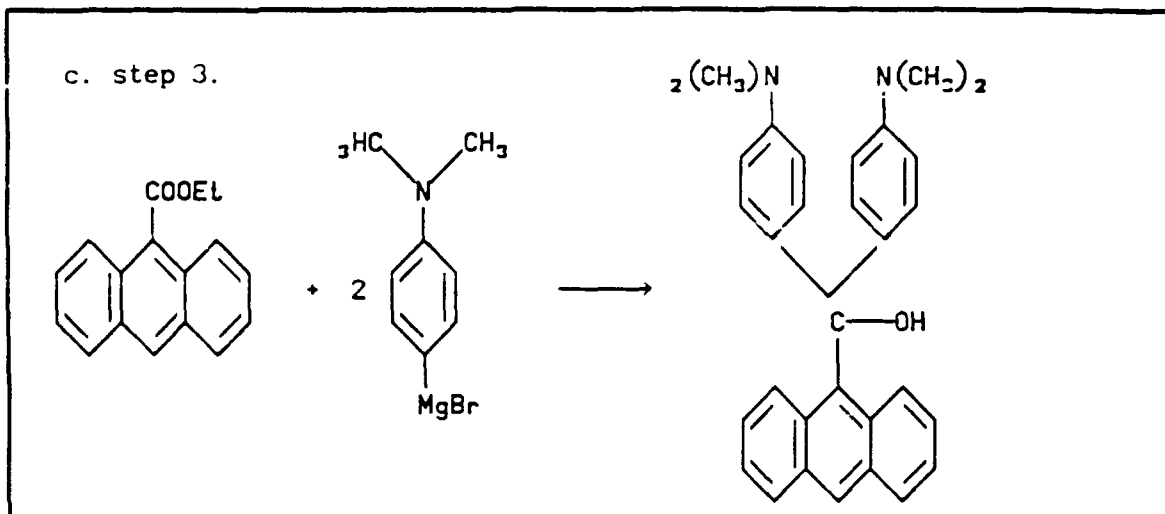


Figure 4. Reaction 3: condensation

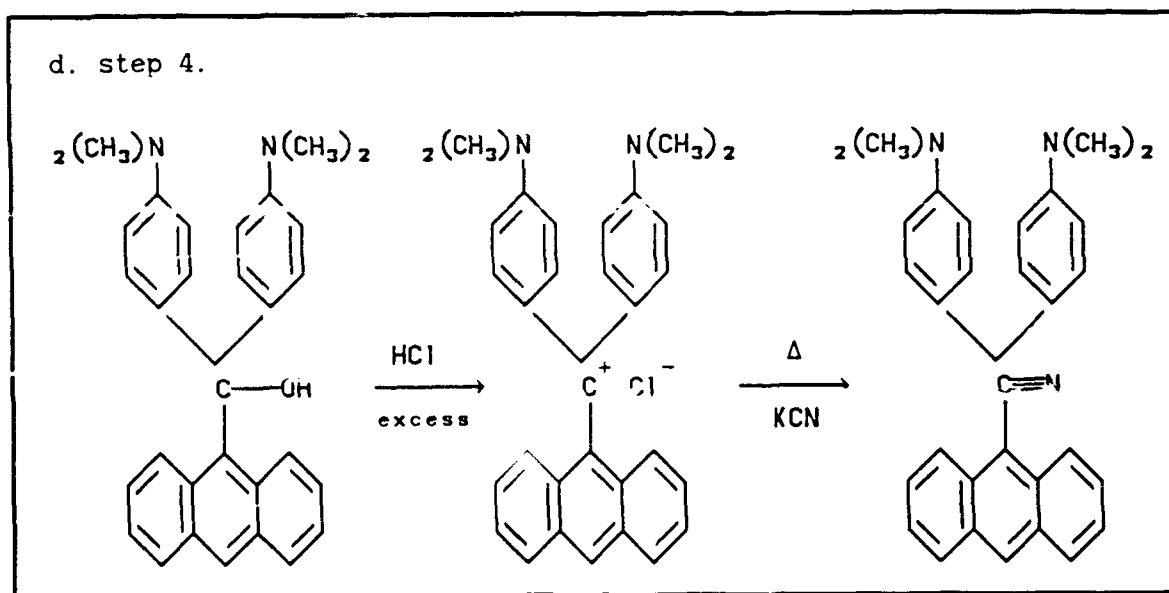


Figure 5. Reaction 4: acid solvation

### 3.1.1. Details of Chemical Synthesis

#### 3.1.1.A. Step 1. Esterification.

There were three methods attempted to produce the ester (see schemes below).

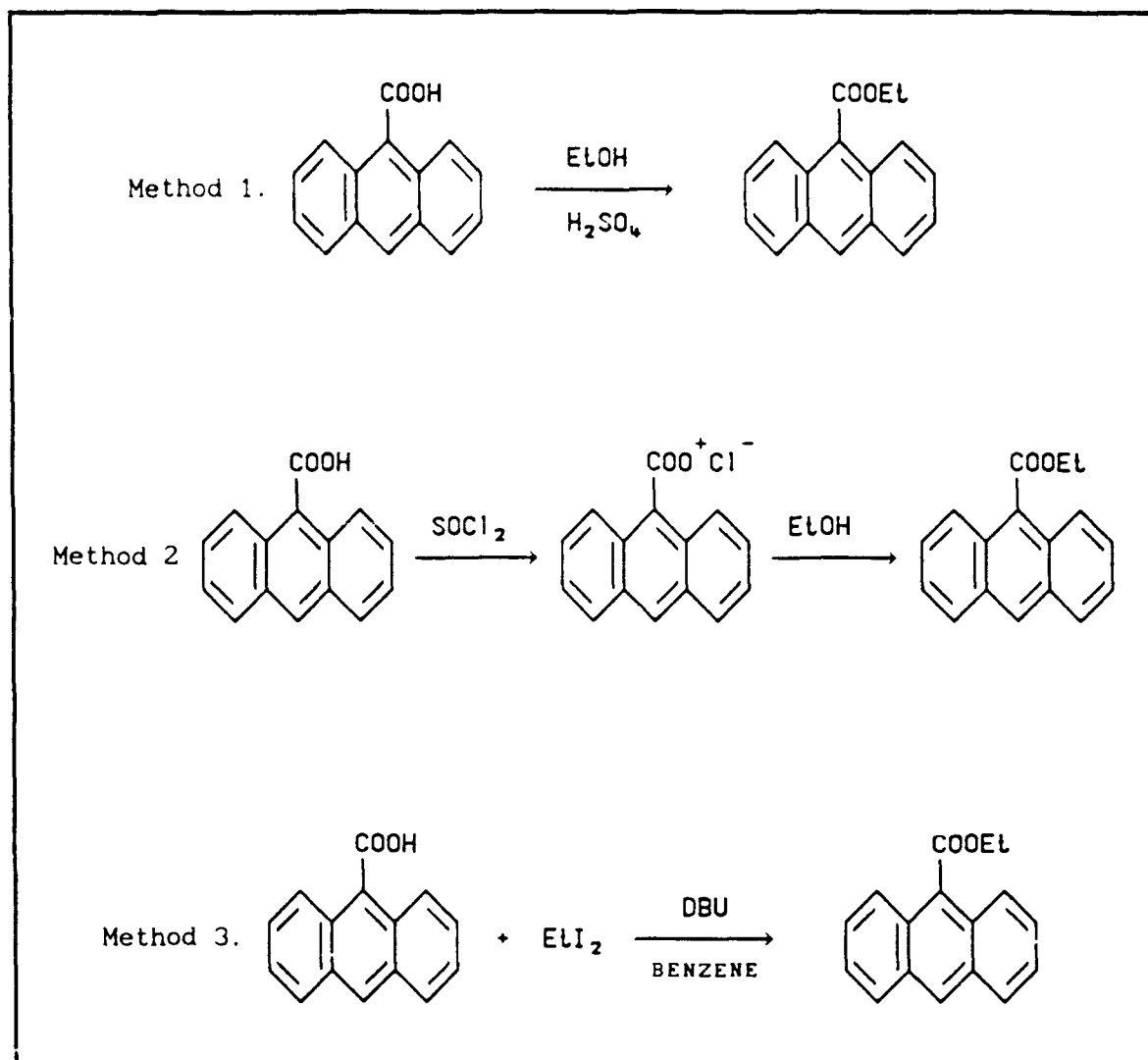


Figure 6. Approach I methods of esterification

It was found that the third method was the most suitable in producing the ester with a yield of ~ 80%. The reaction by-products was low; (DBU (1,8-diazabicyclo[5.4.0]undec-7-ene) hydrohalides, DBU HX) were easily removed by conventional purification techniques.

**Method 1.** The first approach is known as the Fisher-Speier method and is commonly used in the esterification of carboxylic acids. In

this procedure 5g of 9-anthroic acid, 15g of ethanol and 1.5g of concentrated sulfuric acid were mixed in the reaction flask. The solution was refluxed under nitrogen for 4 hrs, after which time approximately half of the remaining ethanol was distilled off. Precipitation was induced by the addition of 30 ml of water to the reaction flask. The precipitant, a yellowish powder with a sweet odor, was collected. The calculated yield was extremely low, only about 8%.

Method 2.<sup>[4]</sup> In the second method, 1g of 9-anthroic acid, 3ml of thionyl chloride ( $\text{SOCl}_2$ ) and 20ml of anhydrous benzene were mixed in a 150ml reaction flask and refluxed for 3 hrs. Excess benzene and thionyl chloride were removed by distillation. The remaining solution was refluxed with absolute ethanol (20ml) for 2 hrs. The solution was allow to cool to room temperature and a crystalline product was collected using vacuum filtration. The yield from this esterification method was again very low (~ 10%). The remaining part of filtrate was characterized as 9-chloroanthracene (mp.  $108^\circ\text{C}$ ). Subsequently, the reaction time of the 9-chloroanthracene with ethanol was increased to 10 and 24 hrs in an attempt to increase the ester yield, but did not change it significantly.

Method 3.<sup>[5]</sup> Equimolar (10 mmol) amounts of ethyl iodide in 5ml of benzene, 9-anthroic acid and DBU were mixed in 15ml of benzene. The mixture was refluxed for 10 hrs and allowed to cool to room temperature. Large needle-shaped crystals precipitated from solution, were filtered out, washed with water and recrystallized twice ( first from heptane and then from methanol ). This method gave an excellent yield ( ~ 80% ) of high purity product, m.p.  $105-106^\circ\text{C}$ .

#### 3.1.1.B. Step 2. Grignard Reaction.

The Grignard reaction proved to be exceedingly difficult to

initiate; however, once initiated the reaction proceeded vigorously. In the first attempt 0.5g non-activated magnesium turnings were covered by ether in a 100ml reaction flask. Subsequently, 3.65g of bromo-diethylaniline was dissolved in ether (5ml) and added dropwise to the magnesium ether solution. The Reaction did not ensue over a 48 hrs refluxing period. It was obvious that magnesium had to be activated to start this reaction.

In order to activate magnesium, a mixture of 1g magnesium, 20ml benzene, 0.5g iodine and 1ml ether was prepared <sup>[6]</sup>. The solution was stirred until the iodine color disappeared and was subsequently distilled to dryness. The remaining residue was removed from the reaction flask and quickly placed in a sealed container to protect it from the ambient atmosphere.

Alternatively, magnesium can also be activated by stirring in the presence of nitrogen <sup>[7]</sup>. In this method, magnesium turnings were stirred in a flask using a teflon-paddle mechanical stirrer under a nitrogen atmosphere for 24 hrs producing finely divided magnesium particles which were used to initiate the Grignard reaction.

It was later found that activated magnesium had no effect on the yield of Grignard reaction prompting an investigation of the "entrainment method" or continuous activation method introduced by Grignard <sup>[8]</sup>. Ethyl bromide, ethyl iodide and iodine were all tried as initiators in the Grignard reaction. It was found that these alkyl halides enhanced the reaction when used in THF, and remained unreactive in an ether solution. This method involved the addition of 1g of magnesium turnings placed in a 100ml reaction flask equipped with a reflux condenser, nitrogen inlet and addition funnel. Approximately 50ml of THF was added and the reactants mixed by bubbling dry nitrogen. The addition of 2 drops of ethyl bromide to the mixture initiated a vigorous reaction. Bromodimethyl aniline (10g) in a THF (10ml) solution was added dropwise to the reaction flask. The addition rate was kept constant with the reaction rate, ie. it was slowed down whenever the reaction slowed. After the addition was finished, the mixture was gently heated to complete the reaction. During the course of the reaction, solution went through a wide range of colors ending up as grey. The reaction was then assumed to be complete. Very small particles of magnesium still remained

in the reaction mixture. The ester was directly added to Grignard solution.

#### 3.1.1.C. Step 3. Condensation Reaction.

This reaction was initiated by the addition of 4g of 9-anthroic acid ethyl ester to the Grignard solution obtained in previous step. The mixture was refluxed for 2 hrs during which time the color changed to rose and then to dark green which contained a yellow precipitate. The solution and precipitate were poured into a acidic aqueous solution (25 g ice and 1 ml  $H_2SO_4$ ) and stirred for 15 minutes in which time the precipitate became soluble. THF was removed by distillation and the compound was extracted with ether. The ether layer was washed with water, a 5% sodium bicarbonate solution and then water once again. It was dried using sodium sulfate and the ether was allowed to evaporate. The residue containing the carbinol was recrystallized from hexane and dissolved in DMSO in preparation for the acid solvation.

#### 3.1.1.D. Step 4. Formation of Anthracene Leucochloride Dye and Anthracene Leuconitrile

Dry HCl was passed through the carbinol DMSO solution from step 3 until a deep green or rose color developed (approx. 30 sec.); nitrogen gas was used to remove any residual HCl. Excess KCN was added to the resulting solution (heated on a steam bath) until the color changed back to yellow indicative of the original carbinol. The solution was cooled and the unreacted KCN was removed by filtration. The filtrate was heated to a boil, fogged by the addition of water and cooled. The pale yellow leuconitrile crystals were filtered off. They became immediately dark blue/green in color once dried; a melting point measurement showed decomposition of this compound at  $230^{\circ}C$ . UV-Vis and IR spectra of leuconitrile are presented in Figure 7a and 7b. Calculated reaction yield for the cyanide conversion step was 80%; the overall yield for the leuconitrile synthesis starting with 9-anthroic acid was less than 3%.

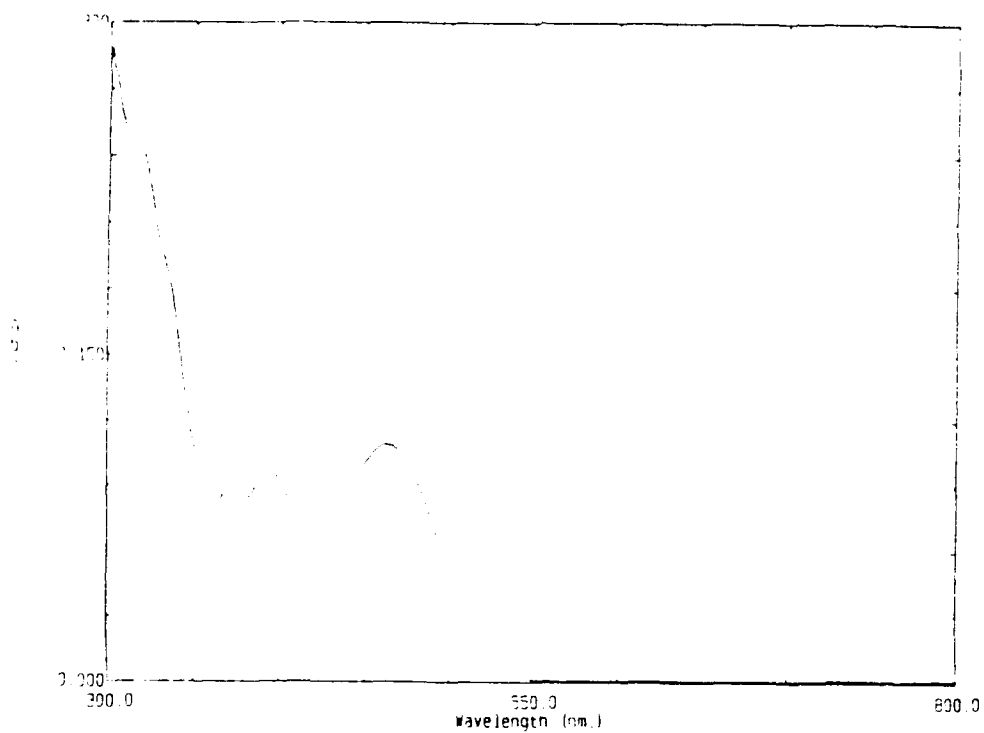


Figure 7a. UV-visible spectrum of anthracene leuconitrile.

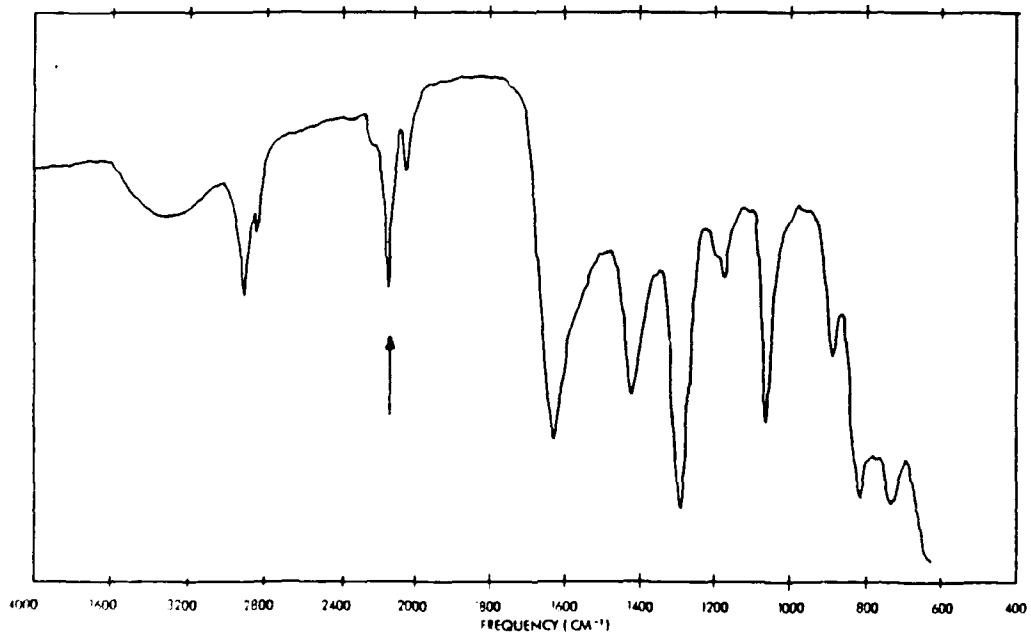


Figure 7b. IR spectrum of anthracene leuconitrile on a Ge prism. Arrow indicates C≡N vibration frequency.

### 3.1.2. Optical evaluation of 9-anthracene leuconitrile

The optical properties of the anthracene leuconitrile were evaluated using two basic techniques: UV-vis spectroscopy and laser studies. The absorption profile of the synthesized compound is very similar to the absorption spectrum of a generic TAML, ie. almost identical with the sum of the individual aryl chromophore groups. The absorption maxima are located in the near UV range and at about 450nm. The exposure of the compound to sun light shifts the maximum in the visible to above 500nm indicative of photochemical ionization and formation of the dye. Light sensitivity of the anthracene leuconitrile is rather remarkable, ie. even a short exposure to the high frequency radiation induces dye formation. It was found that successive scans of the same sample produced slightly different absorption spectra; the detectable shift in the absorption maximum can only be explained by photochemical dissociation of the leuconitrile induced by the spectrophotometer light source.

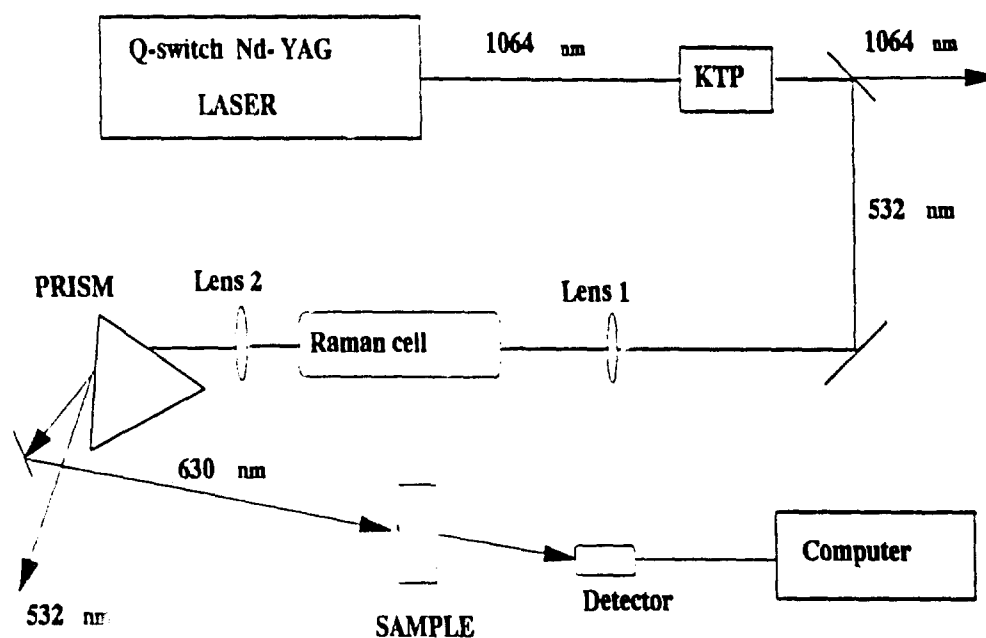


Figure 8. Optical experimental arrangement for laser induced two-photon absorption.

Laser studies were performed in order to evaluate the photoionization of the anthracene leuconitrile at the frequency of two photon absorption. The experimental arrangement (see Figure 8) used in these studies consisted of an actively Q-switched Nd-YAG laser providing 15ns pulses of the fundamental radiation at 1064nm (350mJ/pulse energy at 30Hz repetition rate). A KTP crystal was used to double the fundamental laser frequency. A Raman shifter liquid cell was used to adjust the laser radiation to the anthracene two-photon absorption frequency; it consisted of a 10 cm long glass cell filled with dimethyl sulfoxide (DMSO). The second harmonic of Nd-YAG was used as a pump beam. Due to the large Raman scattering cross-section of DMSO, very efficient stimulated Raman radiation at ca. 630nm could be achieved, with up to 50% conversion efficiency of the pump beam. The pump and Raman frequencies were separated by a highly dispersive prism. The intensity of the Raman shifted beam was controlled by inserting in its path a neutral density filter(s) with a well defined transmittance.

The studies performed on the anthracene leuconitrile carbon tetrachloride solution (1 cm long cell) revealed that the light attenuation did not show the anticipated quadratic power dependency characteristic of two-photon process. For an input intensity range of a few  $\text{kW}/\text{cm}^2$  to about  $500 \text{ MW}/\text{cm}^2$ , the absorption increased by only about 30%. It was determined that there were two contributions to this observation. First, the anthracene leuconitrile sample contained a significant amount of impurities which could not be removed by recrystallization or by extraction methods. The only technique applicable was fractional chromatography, which could only be used to a limited extent due to the poor yield of the synthesis. These impurities caused undesirable single photon absorption leading to thermal effects (sample boiling) which prevented studies from being carried out at higher input intensities and establishing the threshold intensity for two-photon absorption. Second, the compound's light sensitivity resulted in the presence of the photoionized dye form which also led to undesired single photon absorption. In order to avoid any increase in single photon absorption due to the presence of impurities and, perhaps, the compound's photochemical instability, it was decided that the alternative approach be undertaken in an effort to obtain a purer anthracene leuconitrile with a significantly larger yield.



### 3.2. SYNTHESIS: APPROACH II (GENERAL)

Approach 1 provided the expected compound and the expected color changes but produced a very small yield of the leucocyanide compound. Therefore, the second approach, commonly used for the dye production in the agricultural industry<sup>[9]</sup>, was attempted. This method consisted of three major steps, with the last step being basically the same as in approach I. The anticipated advantage of this method was the lesser number of synthetic intermediate products as well as performing the condensation of the aryl group without introducing the troublesome Grignard reaction. The basic synthetic steps of this approach with appropriate reaction schemes are listed below.

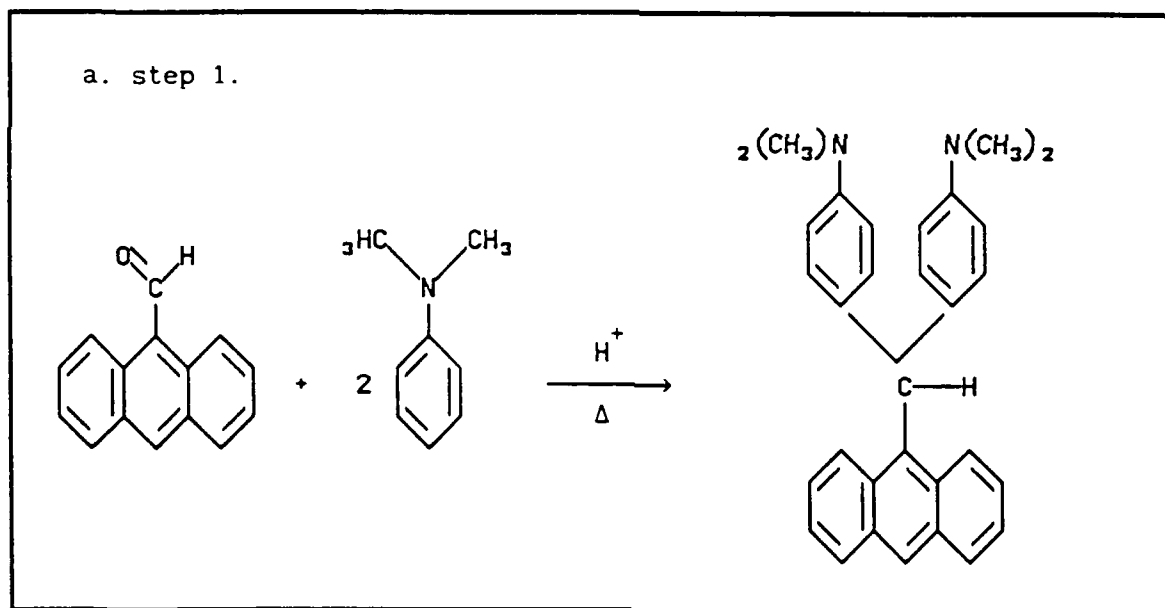


Figure 9. Reaction 5: condensation

b. step 2.

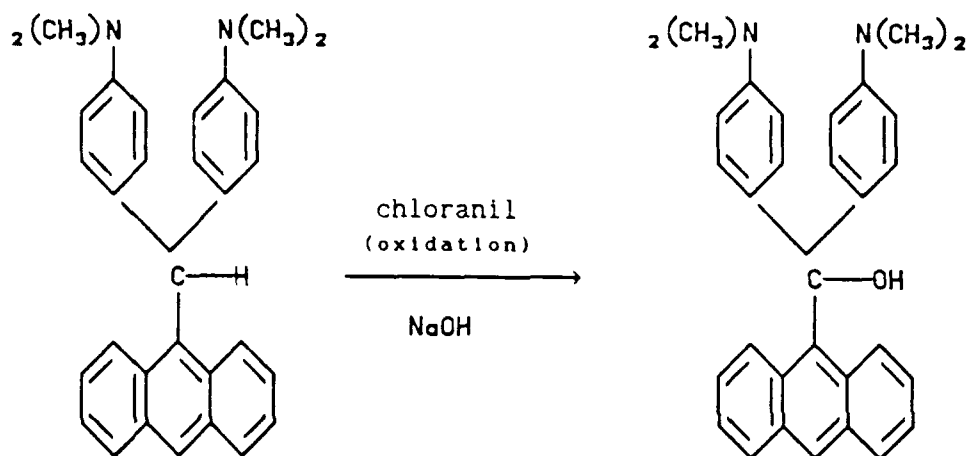


Figure 10. Reaction 6: oxidation

c. step 3.

( see Figure 5. Reaction 4: acid solvation )

### 3.2.1. Details of Chemical Synthesis.

#### 3.2.1.A. STEP 1. Synthesis of Leuco Base.

The triaryl methane was synthesized by routine condensation of the appropriately substituted benzaldehyde with *N,N* dimethylaniline<sup>[2,3]</sup>. The reaction was initiated by adding 5g (0.024 mol.) of 9-anthraldehyde, 50 ml of water and 2.1 ml of  $\text{H}_2\text{SO}_4$  to a 100 ml flask followed by the addition of 4.41 g (0.036 mol) of *N,N* dimethylaniline. It was found that a molar ratio of 3:2 (aldehyde:aniline) gave the greatest yield.

The reaction was carried under reflux for 18 hours. The reaction mixture was then cooled to room temperature and neutralized with a 10 % sodium bicarbonate solution. Approximately 50% of the water was removed by simple distillation; chloroform was subsequently used several times to extract the product and the chloroform solutions combined. The triaryl leuco base and starting reagent were precipitated by the addition of 10 ml water/ethanol to the hot extract. Due to the solubility difference, the first fraction filtered off was largely (~90%) the unreacted aldehyde. The filtrate was heated and another water/ethanol solution added. The product (light yellow needle-shaped crystals) was collected and the procedure repeated until all triarylmethane base was extracted. Each fractional recrystallization produced a more pure sample of the compound evidenced by a narrower melting point (100<sup>0</sup>C). The calculated yield of the reaction was 85%. The IR spectrum of the leuco base is displayed in Figure 12. The leuco base is air sensitive; if exposed to air it would begin to oxidize, changing its color to green. Controlled oxidation was performed using excess chloranil as an oxidant in the absence of air.

#### 3.2.1.B. STEP 2. Oxidation of Leuco Base

Oxidation of the leuco base was completed by reacting it with chloranil: 4 g of chloroanil was added to a leuco base (2 g) ethanol solution (150 ml) and refluxed for one hour under a nitrogen atmosphere causing the color to change to a deep green (a longer refluxing time resulted in the formation of unwanted byproducts eg. dihydrochloranil). Excess chloranil was precipitated by cooling the solution in a ice bath and filtering it out. The addition of 20 ml of water produced a dark green filtrate containing several impurities. Carbon tetrachloride was repeatedly added to the water solution to extract out the impurities until a clear blue solution remained. The solution was heated whereupon 50 ml of hot 10% NaOH was added. The carbinol was extracted with hot carbon tetrachloride and the solution was washed with another hot solution of 10% NaOH; water was subsequently removed by the addition of sodium sulfate. Even though this reaction changed the color of the solution, it was found that the formation of carbinol gave only 10%

yield. The bulkiness of the anthracene and dimethylaniline groups was the most likely reason inhibiting the reaction with the tertiary carbon.

### 3.2.1.C. STEP 3. Formation of Anthracene Leuco Chloride Dye and Leuconitrile

The ionic form of the triarylchloromethane was prepared by bubbling dry  $\text{HCl}_{(g)}$  through a solution of carbinol (.5g) and DMSO (10 ml). The reaction was completed when the solution formed a deep green-rose color. The addition of excess HCl caused the solution to become lighter in color; nitrogen was then bubbled through the solution to minimize unreacted HCl. Potassium cyanide (0.30 g) was added to the heated solution and refluxed (~ 1 hr) until the color was light (back to the original carbinol color). The unreacted KCN was removed by filtration. Water was added to the reheated filtrate to induce crystallization when the solution was cooled; this resulted in very fine white particles that were extracted with carbon tetrachloride and subsequently dried using sodium sulfate. The UV-visible spectra of this solution were

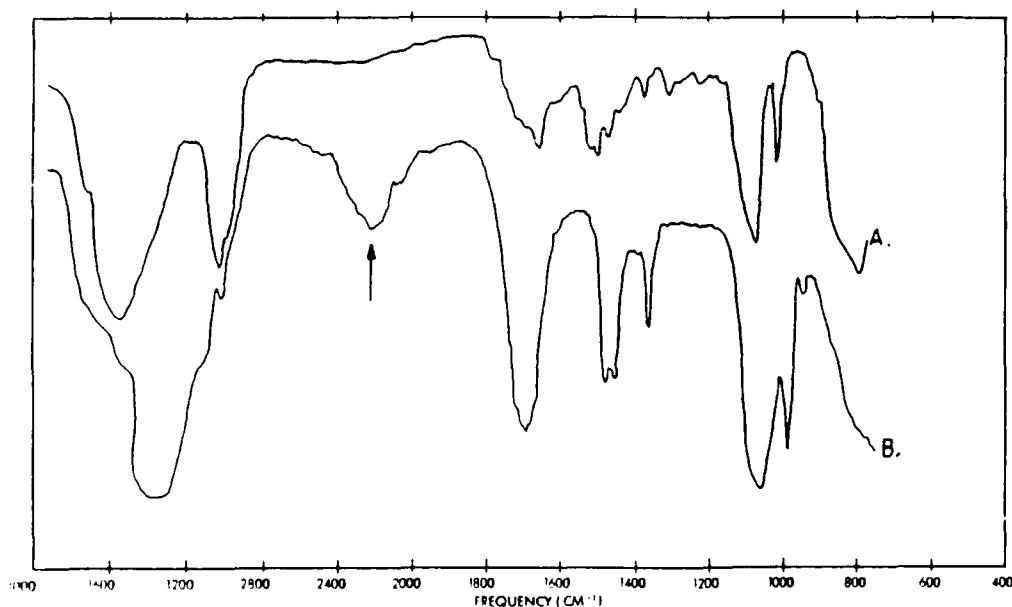


Figure 11. IR spectra of a) carbinol and b) anthracene leuconitrile  
Arrow indicates  $\text{C}\equiv\text{N}$  vibration frequency.

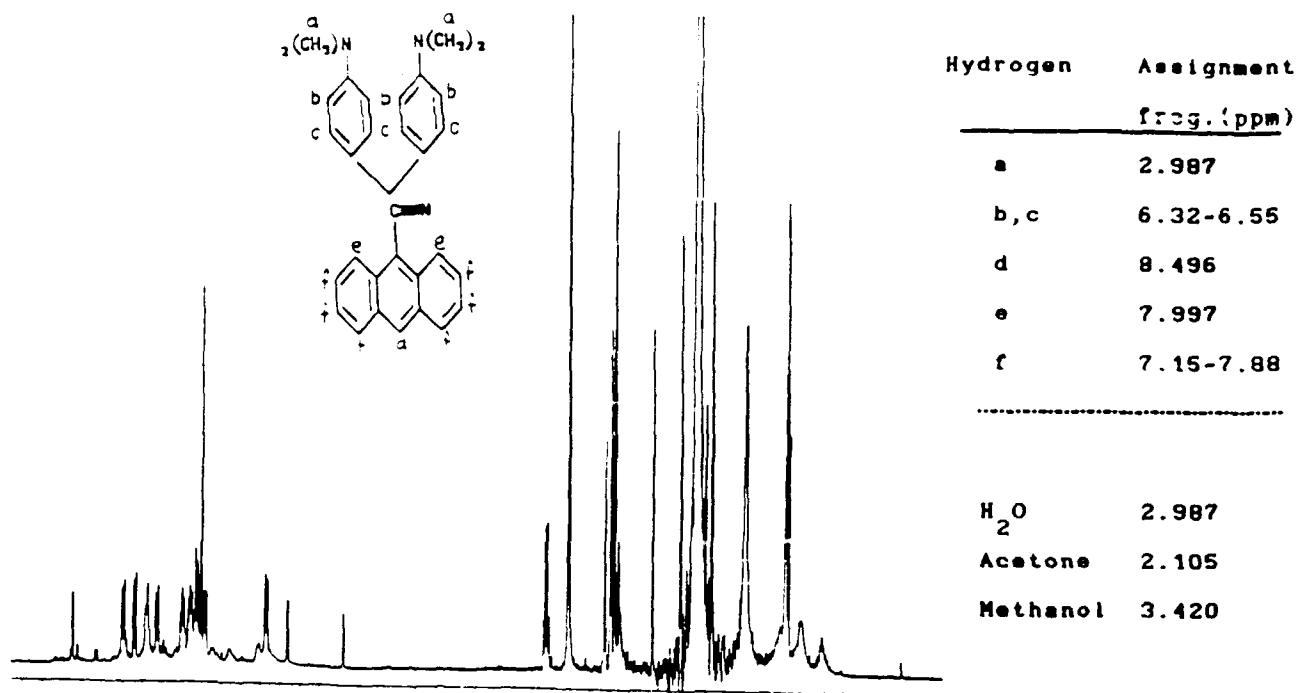


Figure 12. NMR spectrum of anthracene leuconitrile

indistinguishable from that taken from approach I (see Figure 7a). The IR spectra (Figure 11) of anthracene leuconitrile confirms the presence of the cyano functional group. NMR analysis was performed on the final compound in deuterated chloroform. Peak assignments in Figure 12 are consistent with the presence of the final product.

If the carbon tetrachloride was evaporated, the leuco cyanide would covert back to the dye form very quickly. In addition, the dye form would result from the addition of polar solvents (eg methanol, cyclopentanone, etc.) or exposure to white light (sunlight). The yield of step 3 was high (~75%). The overall yield for this approach was again low (ca. 5%) due to the inefficiency of the oxidation step with chloranil. The presence of significantly more sample permitted more extensive purification. Measurement of the melting point showed compound decomposition at  $220^{\circ}\text{C}$  -  $225^{\circ}\text{C}$ , similarly to the leuconitrile compound synthesized in approach I.

### 3.2.2. Synthesis of Malachite Green Leuconitrile

In order to optimize the yield of the final product(s), commercially available malachite green carbinol base was obtained to evaluate the appropriateness and conditions under which previously published methods could be applied. The malachite green was reacted with excess (2x) HCl and then with excess KCN (see step 3); it was found that the anthracene compound behaved similarly to malachite green leuco compound. Upon optimizing the reactions for malachite green, it was learned that a

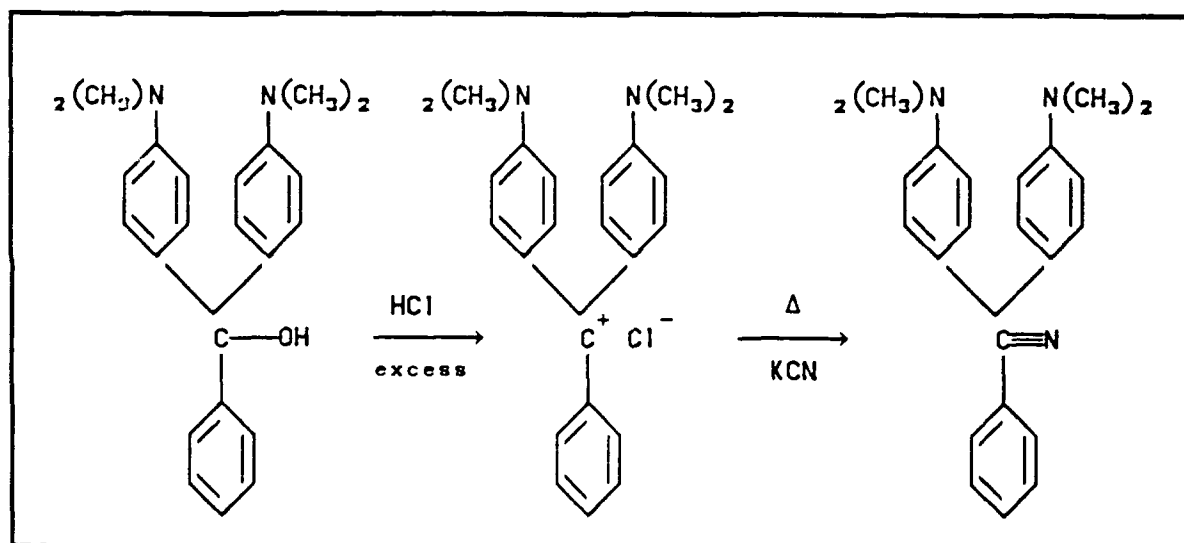


Figure 13. Synthesis of malachite green leuconitrile.

precise amount of HCl was crucial to the successful synthesis of the leuconitrile. This information was applied to the synthesis of anthracene leuconitrile with satisfactory results. Both leuconitrile and malachite green leuconitrile remained colorless or slightly yellow in carbon tetrachloride and benzene while in more polar solvents, such as methanol and cyclopentanone, the respective dye colors emerged. In

addition, both the malachite green leuconitrile and the anthracene leuconitrile became colored upon exposure to sunlight.

Since the malachite green was bought oxidized and both compounds (malachite green leuconitrile and anthracene leuconitrile) behaved similarly, it was determined that the oxidation of the anthracene leuco base presented the most difficulty.

### 3.2.3. Optical characterization.

The optical methods used to characterize 9-anthracene leuconitrile were the same as described in Section 3.1.2.. The product of Approach II was in greater yield and could therefore be more highly purified. Since this sample had the same photochemical instability as that from approach I, it was determined that the impurities did not contribute to the overall tendency to photoionization. It does indicate that leuconitrile sensitivity to photoionization by very low intensity white light (sun light) is an intrinsic property of this class of compounds. Figure 12 depicts the absorption spectra of an anthracene leuconitrile carbon tetrachloride solution exposed to sun light for different periods of time; it is obvious that the formation of a photoionized compound (dye) takes place. It is also certain that the presence of the dye form of the leuconitrile significantly contributes to the undesired single photon absorption and induces thermal effects. This property should be avoided in any kind of optical device because of the characteristically slow response times and possible damage to the active media. It should be emphasized that the reconversion from the dye to the leuconitrile form required heating in excess of 70°C in the dark for a period of minutes.

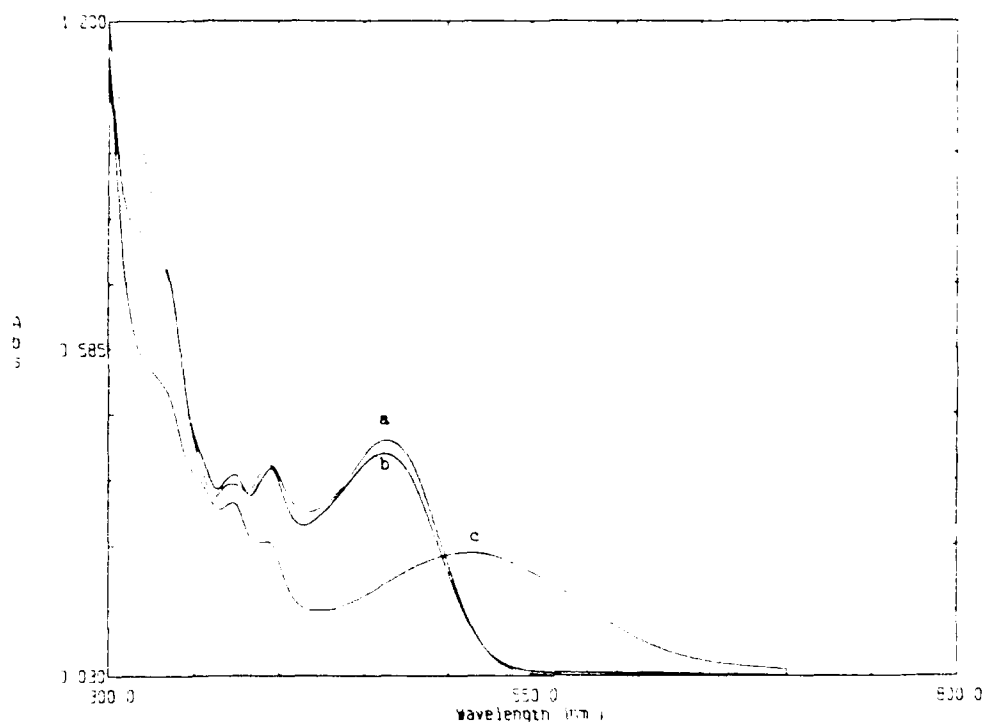


Figure 14. UV-visible spectra of anthracene leuconitrile exposed to different amounts of white light (sunlight): a) unexposed, b) 5 minutes and c) 45 minutes

Serious attempts were undertaken to incorporate anthracene leuconitrile in polymer (polystyrene) and sol-gel glass (silica and silica/titania) matrices in an effort to determine whether these composites would lend photochemical stability to the compound. Previous work with other photochemically active chemicals (laser dyes, saturable absorbers, etc.) have indicated that these matrices can provide unique molecular environments evidenced by, for instance, elevated decomposition temperatures. Unfortunately, the leuconitrile compound predictably converted to the dye form when exposed to small concentrations of polar solvents which are inevitably present in sol-gel



processing. The effects of minimal amounts of methanol on the UV-visible spectra can be seen in Figure 13. The fabrication of leuconitrile doped polymer films (without polar solvents) did not lead to the dye form until the films had been dried. The compound in all solid states (crystals or dispersed in polymer matrices) quickly converted to the dye form upon the release of solvent. In addition, the reconversion to the leuconitrile form of the compound in these polymer films.

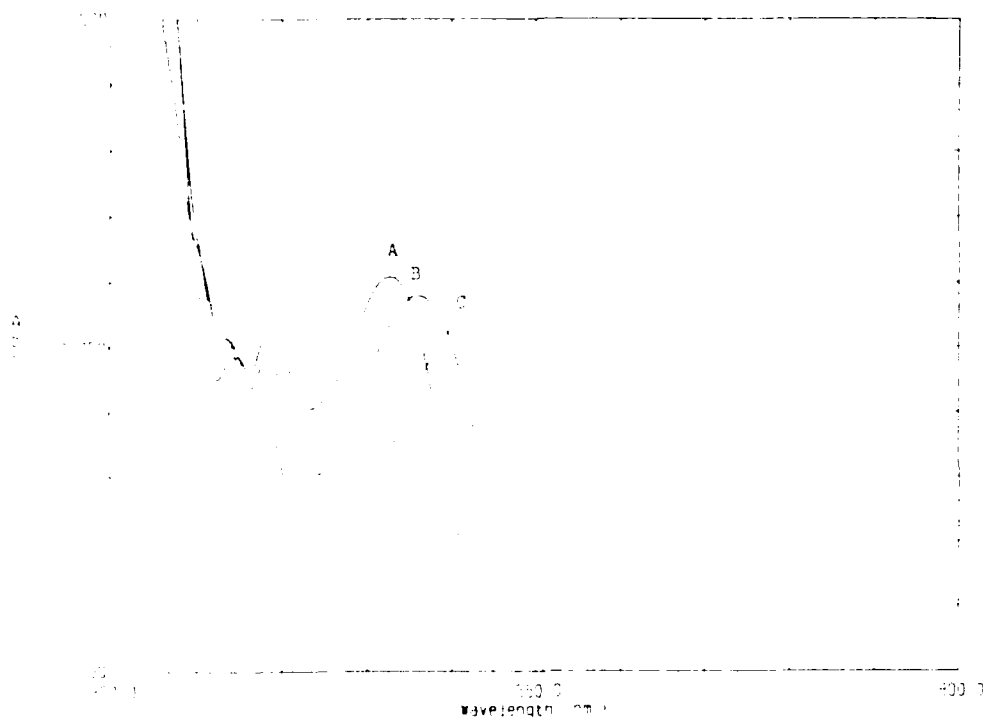


Figure 15. Effect of methanol on the UV-visible spectra of anthracene leuconitrile: a) no MECH, b) 2 drops MECH/cuvette and c) 20 drops MECH/cuvette

#### 4. Conclusions and Recommendations

The synthesis of a compound incorporating a nonlinear two photon absorbing functional group adjacent to a photoreactive moiety in an effort to obtain a material that could function to protect human vision and light sensitive equipment from laser based weapons is a sound approach. The use of organic chemicals in this application enables one to tailor the optical response to meet particular device requirements.

The proposed compound has been shown to be insufficiently photochemically stable for employment in anticipated applications (laser shielding of human vision, sensitive photochemical equipment and optical power limiters). The reversion of the absorbing to transparent forms of the studied compound were also insufficiently slow to be functional in anticipated devices. Times of minutes and temperatures in excess of 70°C were required to restore material transparency. In addition, the compounds sensitivity to polar solvents significantly limits its processability.

In light of these findings, Laser Photonics Technology, Inc. has chosen not to submit a Phase II proposal. While the approach is fundamentally sound, subsequent steps to achieve the proposed goals are not immediately obvious. It is felt that a Phase II effort at this time would not be sufficiently directed at overcoming the challenges and could not guarantee reasonable success.

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## Appendix A. License Rights Legend

### LICENSE RIGHTS LEGEND

Contract No.F 49620-90-C-0082

Contractor or subcontractor Laser Photonics Technology, Inc.

For a period of two (2) years after the delivery and acceptance of the last deliverable item under this contract, this technical data shall not, without the written permission of the above Contractor be either (A) used, released or disclosed in whole or in part outside the Government, (B) used in whole or in part by the Government for manufacture, or (C) used by a party other than the Government. After the expiration of the two (2) year period, the government may use, duplicate, or disclose the data, in whole or in part and in any manner, for Government purposes only. All rights to use or duplicate the data in whole or in part for commercial purposes are retained by the contractor, and others to whom this data may be disclosed agree to abide by this commercial purposes limitation. The Government assumes no liability for use or disclosure of the data by others for commercial purposes. This legend shall be included on any reproduction of this data, in whole or in part.