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# THE SYNTHESIS AND STUDY OF THE ABSORPTION AND EMISSION PROPERTIES OF SOME NAPHTHYL SILANES IN THE ULTRA-VIOLET REGION

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# THE SYNTHESIS AND STUDY OF THE ABSORPTION AND EMISSION PROPERTIES OF SOME NAPHTHYL SILANES IN THE ULTRA-VIOLET REGION

THESIS

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by

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## Preface

It has been my purpose in writing this report to add to the store of knowledge currently available on organic compounds and their basic luminescent properties. The naphthylsilanes prepared for this study show many characteristics of a good scintillator for the detection of ionizing radiation. The ultra-violet absorption spectra of these compounds can be used in identifying compounds, calculating energy levels of excitation, and for obtaining information on the interaction of molecular orbitals. These compounds also yield information as to the role of the silicon atom in the luminescence process when attached to conjugated molecular systems.

I wish to express my gratitude to Dr. Leonard Spialter of the Chemistry Branch of the Aeronautical Research Laboratory for the patience, advice, and council which he so graciously gave.

I am also indebted to Dr. George John of the Physics Department at the Institute of Technology for his advice and help, and I wish to express my thanks for his encouragement throughout this study.

Calvard S. Allen

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## Abstract

Two synthesis schemes are used to prepare eight related naphthylsilanes. The basic absorption and emission properties of these compounds are investigated in the ultra-violet region. These properties include molecular extinction coefficient determinations, fluorescence of glass silanes, fluorescence in cyclohexane and EPA at 298°K and 77°K, and phosphorescence in EPA at 77°K. Also mean lifetimes of phosphorescent bands were determined.

Molecular extinction coefficient calculations indicate the 1-naphthylsilanes absorb light in direct proportion to the number of naphthalene molecules attached to the silicon atom. No apparent correlation in the absorption of the 2-naphthylsilanes exists.

Fluorescence spectra of the 1-naphthylsilanes indicate bands comparable to those of naphthalene. Energy transfer between naphthalene molecules in the 2-naphthylsilanes is indicated and the emission bands are at longer wavelengths than those of naphthalene.

Phosphorescence for each naphthylsilane occurs at approximately 500 $m\mu$, the same as the wavelength for phosphorescence of naphthalene. Mean phosphorescent lifetimes are comparable with previous glass forming silanes.

# THE SYNTHESIS AND STUDY OF THE ABSORPTION AND EMISSION PROPERTIES OF SOME NAPHTHYL SILANES IN THE ULTRA-VIOLET REGION

## I. Introduction

Extensive research by workers at Aeronautical Research Laboratories has been done on the chemistry of silane compounds. Studies on the mixed phenyl- and p-biphenylyl-substituted silanes show that these compounds fluoresce in the visible range when excited by either ultraviolet light or ionizing radiation (Ref 6:94-96). These studies also indicate the potential value of silane compounds as scintillators. Recently, new naphthylsilane compounds have been made which show physical characteristics similar to those of the biphenylylsilanes. The biphenylylsilanes and naphthylsilanes are white solids which form colorless fluorescent glasses when the molten material is cooled below their melting points. The property of forming glasses facilitates the fabrication of scintillators of any desired shape. It was of interest, therefore, to investigate the basic luminescence of the naphthylsilanes.

The purpose of this report is to present and interpret the results of a research investigation of the basic absorption and emission properties of eight related naphthylsilanes. In particular, this work was undertaken to obtain information concerning the effect of the silicon atom in the luminescence process, to obtain information about the position effect of the silicon atom when this atom is attached to a conjugated molecular system, and to add to the current knowledge on the value of silane compounds as scintillators.

## Results of Previous Studies

Numerous organic crystals have been studied as scintillators. To date, the most useful of these materials are anthracene and trans-stilbene (Ref 16:168). Spialter (Ref 18:6227-6231), in 1955, published a report which outlines the synthesis of an entire family of tetraaryl silanes. These compounds showed the property of forming luminescent glasses. Subsequent studies by Weis and John (Ref 21:23-24) led to the belief that a silane compound could be developed as a new scintillator which was as good as, or better than anthracene but which had glass-forming properties.

Luminescence of Tetraaryl Silanes. Downs and Smith (Ref 18:6227-6231) were the first investigators to report the detection properties of tetraaryl silanes, and later, Weis (Ref 20) completed the study of the detection properties of the available tetraaryl silanes relative to an anthracene standard. Weis reported that the pulse heights of the tetraaryl silanes are about 40% to 50% of the pulse height of anthracene, and that the silane glasses are about 70% as efficient as anthracene for beta detection.

The first completed work on the basic luminescent properties of the tetraaryl silanes was done by Polk (Ref 15). A similarity of the emission characteristics of the biphenylyl-substituted silanes to the corresponding characteristics of biphenyl was found by Polk. This similarity indicated that the biphenylyl group was most responsible for luminescence in the tetraaryl silanes.

Naphthyl Silanes. Part of Polk's work was an attempt to synthesize an anthracenylsilane in order to incorporate the glass-forming properties of the silanes with the scintillation efficiency of anthracene. The desired compound was not obtained. However, Polk's method of synthesis seemed readily applicable to the synthesis of naphthylsilanes. These naphthylsilanes would serve as model compounds similar to anthracenylsilanes, and an investigation of the luminescent properties of the naphthylsilanes would be pertinent to later work involving anthracenylsilanes.

Spialter, Towers, and Newing (Ref 19) had previously prepared four naphthyl silanes: triphenyl-1-naphthylsilane, triphenyl-2-naphthylsilane, di-1-naphthyl phenyl ethoxy silane, and trimethyl-1-naphthylsilane. These workers graciously provided samples of these compounds for this investigation. Additional related molecules were synthesized by this author for this research study.

Luminescence of Naphthyl Compounds. A search of the literature revealed no previous work on the luminescence of any of the compounds prepared for this investigation, although much work has been done on naphthalene and some of its simple derivatives.

An example of the efficiency of some naphthyl compounds as scintillators was shown by Heller (Ref 10:25). He devised a quantum mechanical method for the evaluation of the energy transfer, fluorescence and scintillation efficiencies of solutions of aromatic hydrocarbons in benzene and alkylbenzenes. Heller examined many naphthalene compounds by this method, and reported their efficiency to be as great as 50% that of anthracene.

## Scope of Study

In this study, the compounds prepared by Spialter, Towers, and Newing were used as well as four compounds synthesized by this author. These compounds are diphenyl di-1-naphthylsilane, diphenyl di-2-naphthylsilane, di-1-naphthyl diethoxysilane, and tri-1-naphthyl chlorosilane.

Specific areas of study considered were:

(1) Synthesis of compounds.

(2) Determining the absorption spectrum of each compound in cyclohexane at 298°K.

(3) Determining the fluorescence and activation spectrum of each compound in EPA at 298°K and 77°K, in cyclohexane at 298°K, and the spectra of the glass-forming silanes as a glass at 298°K.

(4) Determining the phosphorescence spectrum and the mean phosphorescence lifetime of each compound in EPA at 77°K.

## Format of Report

The first portion of this report is a review of those aspects of luminescence theory pertinent to this investigation. The second section deals with the synthesis of the naphthylsilanes, while the third section deals with the equipment used and the experimental techniques needed to obtain results. The fourth section presents results, while a discussion of these results and a presentation of conclusions is made in the fifth section. The sixth section deals with work which can be done to further the work done in this paper.

The appendices contain the experimentally determined absorption and emission spectra of each compound, correction curves for the emission spectra and an example of the curves used to calculate the mean phosphorescent lifetimes.

## II. Theory

When light passes through any homogeneous transparent medium it emerges diminished in intensity. Part of the light may be scattered at the surface, part scattered in the interior, and part regularly reflected at the surfaces. The rest of the light which is lost is said to be absorbed. It may be transformed into heat, or into fluorescent or phosphorescent light of wavelengths differing from its own; or it may cause photochemical action.

Organic solids used as scintillators for the detection of ionizing radiation behave much the same way in the emission of light from high energy particles as they do in the emission of light from ultra-violet excitation. Therefore, the use of ultra-violet light for excitation yields information pertinent to scintillation studies.

As mentioned in the introduction, the primary reason for this investigation was the use of a luminescence study to obtain a variety of information on each compound. This information may establish the basis for further work which will use these compounds as scintillators. Therefore, the theory which is pertinent to this investigation is the basic absorption and emission of light by organic compounds.

## Absorption of Light

Laws of Light Absorption. There are two principal laws by which light is said to be absorbed in a medium. The first of these is Lambert's law, which states that the proportion of light absorbed by a transparent medium is independent of the incident light and that each successive unit layer of the medium absorbs an equal fraction of the light passing through it (Ref 7:6).

This law mathematically stated is

$$I = I_o e^{-\alpha L}$$

where $I_o$ = intensity of the incident light

$I$ = intensity of the transmitted light

$L$ = thickness of the layer (in cm.)

$e$ = the base of natural logarithms

$\alpha$ = absorption coefficient.

It is more common and convenient, however, to use logarithms to the base 10 instead of to the base e, and on this base the absorption coefficient $\alpha$ is converted into the so-called Bunsen and Roscoe extinction coefficient K. Thus

$$I = I_o 10^{-KL}$$

It is apparent that the coefficients $\alpha$ and K have units of reciprocal length and do not directly contain a concentration factor. The relationship of the absorption coefficient to concentration term is obtained from Beer's law. It states that the light absorption is proportional to the number of molecules of absorbing substance through which the light passes (Ref 7:6).

Lambert and Beer's laws are combined to yield the equation used for calculating the molecular extinction coefficient $\epsilon$.

$$\log_{10} I_o/I = \epsilon cL = E$$

where $\epsilon c = K$

$c$ = concentration in gram mole/liter

$E$ = optical density

Energy States. It has been shown experimentally that molecules of simple structure in which an extensive resonance conjugation of rings exists, absorb and emit light very efficiently (Ref 17:670-715). The present theory of light absorption is based on the structure of these molecules.

In the formation of molecules, interaction between atoms leads to the formation of "orbitals". An orbital is defined as a region in space characterized wave mechanically by a wave function and a discrete energy. The wave function is related to the spatial probability distribution of an electron within the orbital (Ref 15). An excellent review of the bonding which leads to the delocalizing of the electrons in molecules to form orbitals is given by Polk (Ref 15) and will not be repeated in this study.

The lowest energy state (ground state) of an orbital in an ordinary organic molecule is a singlet state, meaning that the two electrons comprising this state have anti-parallel spins. The electrons are thus ordinarily paired in this lowest energy state, two per orbital, according to the Pauli exclusion principle. Higher energy states or excited states arise when these electrons absorb energy and a transition occurs to a higher unoccupied orbital.

Although the ground state of an organic molecule is usually a singlet state, the excited states may be either singlet or triplet. The triplet state is a state in which two electrons spins are parallel, and are not ordinarily populated by a direct transition from singlet ground state because such a transition would violate the $\Delta s = 0$ selection rule (Ref 15:20). However, these states are populated by an energy transfer process which is discussed later.

## Emission of Light

*Fluorescence and Phosphorescence.* In present day spectroscopic practice, singlet states for complex molecules are denoted by $^1\Gamma$, $^1\Gamma^*$, $^1\Gamma^{**}$, and triplet states by $^3\Gamma^*$, $^3\Gamma^{**}$, $^3\Gamma^{***}$. The symbol $\Gamma$ is an arbitrary term symbol, and the asterisks indicate simply that the states are different (usually designating an excited state). The symbol $\Gamma^* \longleftarrow \Gamma$ denotes absorption, $\Gamma^* \longrightarrow \Gamma$ denotes emission, and $\Gamma^* \rightsquigarrow \Gamma$ denotes radiationless transitions with the state of highest energy placed first in order (Ref 12:401).

Excitation to the triplet state $^3\Gamma^*$ almost always involves primary absorption to one of the upper excited singlet states followed by rapid vibrational cascade to the vicinity of the zero point level of the $^1\Gamma^*$ state. From here, either normal fluorescence can occur ($^1\Gamma^* \longrightarrow {}^1\Gamma$) or there may be spontaneous intersystem crossing ($^1\Gamma^* \rightsquigarrow {}^3\Gamma^*$, internal conversion or spin-flip), followed by vibrational cascade to the zero-point level of the $^3\Gamma^*$ state and subsequent spontaneous phosphorescence ($^3\Gamma^* \longrightarrow {}^1\Gamma$).

In some cases, both fluorescence and phosphorescence occur simultaneously with sufficient intensity that both are observable (Ref 3:25-45). In this case, the resulting radiation is usually called "total luminescence", "full luminescence", or "total emission"; further distinction being made by means of lifetime or wavelength measurements.

Most phosphorescence lifetimes are in the range of 20 seconds to $10^{-3}$ seconds, however, some are much shorter. For example, p-dibromobenzene has strong green phosphorescence with a lifetime of 3.3 $10^{-4}$ seconds and fluorescence lifetime of approximately $10^{-5}$ seconds (Ref 2:24). Most fluorescence lifetimes are between $10^{-6}$ and $10^{-9}$ seconds.

The wavelengths of phosphorescence are usually longer than that of fluorescence, since the potential energy difference between the $^1\Gamma^*$ and $^1\Gamma$ states is always larger than that between the $^3\Gamma^*$ and $^1\Gamma$ states. Figure 1 is a potential energy diagram of the three lowest electronic states of a complex molecule depicting potential hyper surface cross-sections along a critical coordinate. After primary absorption (A), fluorescence may occur (F); and in addition, radiationless inter-system crossing (spin-flip) followed by phosphorescence (P).

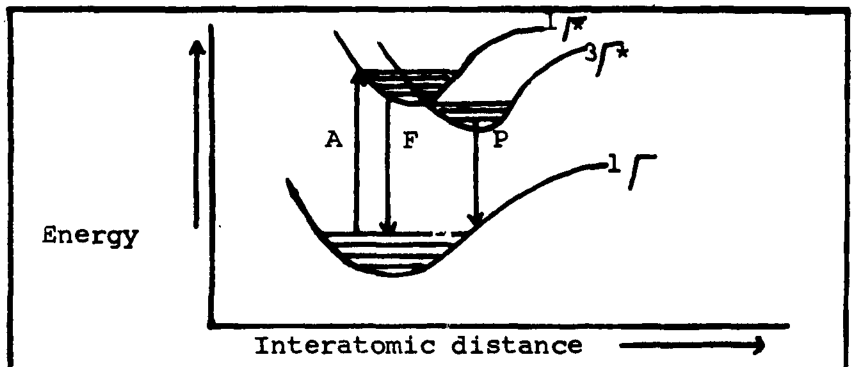


Fig. 1

Electronic Transitions

## Non Radiative De-Excitation

Radiationless transitions occur after energy has been absorbed and an electron has occupied an excited state. Electrons in the excited state $^1\Gamma^{**}$ can dissipate a portion of their energy in one or more of the following ways (Ref 4:2-11).

(1) $^1\Gamma^{**}$ (high vibrational level) $\rightsquigarrow$ $^1\Gamma^{**}$ (low vibrational level) called thermal stabilization.

(2) $^1\Gamma^{**}$ $\rightsquigarrow$ $^1\Gamma^{**}$ called singlet-singlet internal conversion.

(3) $^1\Gamma^{**}$ $\rightsquigarrow$ $^3\Gamma^{**}$ called singlet-triplet internal conversion.

(4) $^1\Gamma^{**}$ $\rightsquigarrow$ $^1\Gamma$ called internal quenching.

The energy in the low vibrational levels of $^3\Gamma^{**}$ can be lost by (Ref 4:2-11)

(1) $^3\Gamma^{**} \rightsquigarrow {}^1\Gamma^{*}$ with thermal stabilization.

(2) $^3\Gamma^{**} \rightsquigarrow {}^3\Gamma^{*}$ with thermal stabilization.

(3) $^3\Gamma^{**} \rightsquigarrow {}^1\Gamma$

All of these transitions mentioned above serve to convert some or all of the absorbed excitation energy into heat rather than light.

## Environmental Effects

Reabsorption of Emitted Light. Although the preceding discussion was limited to a single molecule, the theory must be extended to a complete system such as thick samples or compounds in solution.

In thick samples as well as compounds in concentrated solutions, reabsorption of emitted light by the compound itself is quite predominate. Even in crystals with a thickness of a few microns, the probability of absorption of emission corresponding to $^1\Gamma^{**} \longrightarrow {}^1\Gamma$ or $1\Gamma^{***} \longrightarrow {}^1\Gamma$ transition is very high. (Ref 4:2-11).

Emissions corresponding to a transition $^1\Gamma^{*} \longrightarrow {}^1\Gamma$ are also quite vulnerable to reabsorption. This reabsorption is evidenced by spectral overlap between the absorption spectrum and emission spectrum.

Temperature Effects. At low absolute temperatures, the higher thermally excited vibrational levels of an organic molecule are largely depopulated. This character gives rise to sharper spectral structure. Also at low temperature, decay times are decreased and quantum efficiencies are increased. Sharper spectra, decrease in decay times, and better quantum efficiencies are all brought about by the narrowed vibrational levels.

Under ordinary circumstances, the probability of quenching the long-lived triplet excited state in organic molecules by collision is high. Therefore, phosphorescence can only be observed under conditions which isolate the molecules from one another long enough for emission to proceed. Cooling to $77^{\circ}K$ and forming a rigid media allows phosphorescence to be observed in most compounds. Cooling also reduces high vibrational levels and thus reduces the chances of internal quenching.

## III. Synthesis

Gilman (Ref 9:4640-4644) was one of the first chemists interested in the synthesis of 1-naphthylsilane compounds. Gilman's work concerned the steric factors associated with reactions involving the 1-naphthylsilane compounds. He presented two general methods for making the silane compounds: halogen-metal interconversion and metal replacement of halogen. Gilman's methods were used in this study and extended to the 2-naphthylsilane compounds as well. For simplicity, the halogen-metal interconversion will be referred to as the indirect method and the metal replacement of halogen as the direct method.

The reaction scheme for each method is as follows:

(direct method) $C_{10}H_7Br + 2Li \longrightarrow C_{10}H_7Li + LiBr$
(indirect method) $n\text{-}C_4H_9Br + 2Li \longrightarrow C_4H_9Li + LiBr$
$C_4H_9Li + C_{10}H_7Br \longrightarrow C_{10}H_7Li + C_4H_9Br$

All reactions involving organometallic reagents were performed in an atmosphere of nitrogen in a three-neck flask fitted with a reflux condensor, motor stirrer with a ground glass seal lubricated with silicon grease, and a nitrogen inlet tube. Product melting points were determined on a Koeffler Melting Point apparatus and yields are calculated on the basis of the silicon compound used as a starting material.

## 1-Naphthyllithium (Indirect Method)

1-naphthyllithium is the necessary reactant needed to react with the silicon compound to yield the final product and a typical preparation is as follows.

To a solution of 8.6 grams of lithium metal in 200 ml. of ether was added 68.5 grams of n-butyl bromide in 100 ml. of ether. The flask was cooled to -10°C with a dry ice-acetone mixture while the n-butyl bromide was added at a uniform rate over a 30 minute period. The reaction was assumed to have gone to completion after no lithium metal was observed in the flask. To this solution was added 0.6 moles of 1-bromonaphthalene. The internal temperature was kept at 0 ± 5°C with the dry ice-acetone bath. The time for complete addition was 15 minutes and the mixture was allowed to stir an additional 5 minutes before use.

In like manner, the 2-naphthyllithium was made from 2-bromonaphthalene.

## 1-Naphthyllithium (Direct Method)

To a solution of 1.32 moles of lithium metal in 100 ml. of ether was added 0.6 moles of 1-bromonaphthalene in 200 ml. of ether. An ice bath was used to maintain the internal temperature at 0°C. The reaction was assumed to have gone to completion when no lithium metal was observed in the flask. The resulting 1-naphthyllithium compound was used within 5 minutes of preparation.

In like manner, the 2-naphthyllithium was made from 2-bromonaphthalene.

## Diphenyl Di-1-Naphthylsilane

To an ethereal solution of 0.6 moles of 1-naphthyllithium made by the direct method, was added 0.3 moles of diphenyl dichlorosilane at room temperature and stirred for 24 hours. Water was then added to the mixture to react with any excess lithium metal and the ether layer was then separated by use of a separatory funnel.

The ether layer was dried with magnesium sulfate and then reduced in volume by evaporation. An equal amount of petroleum ether was added to the solution and the mixture was set aside for crystallization to occur.

After 24 hours, white crystals formed in the solution and were collected. One gram of impure product was obtained and was recrystallized from petroleum ether. The yield of pure product was 0.25 grams (.25% of theoretical), melting at 194-195°C.

## Diphenyl Di-2-Naphthylsilane

The diphenyl di-2-naphthylsilane was made by use of the same procedure used in the synthesis of diphenyl di-1-naphthylsilane. The 2-naphthyllithium instead of 1-naphthyllithium was used. The yield of pure product based on the phenyl chlorosilane used was 20%. Diphenyl di-2-naphthylsilane was recrystallized from petroleum ether and melted at 162-163°C.

## Tri-1-Naphthyl Chlorosilane

The direct procedure was used to make 1-naphthyllithium and a typical synthesis of tri-1-naphthyl chlorosilane is as follows.

To a solution of 1.07 moles of 1-naphthyllithium in 200 ml. of ether was added 0.3 moles of freshly distilled silicon tetrachloride in 200 ml. of dry ether. Addition was done at such a rate as to keep the internal temperature between 0°C and -5°C. Stirring was continued for two hours at this temperature before the mixture was poured onto 500 ml. of dilute hydrochloric acid. The organic layer was washed with water and the solvent removed by evaporation. The organic layer deposited 80.0 grams of crude tri-1-naphthyl chlorosilane.

The product was recrystallized three times from methylcyclohexane. The yield of pure tri-1-naphthyl chlorosilane was 50% of theoretical. The compound melted at 210-211°C.

## Di-1-Naphthyl Di Ethoxysilane

A solution of 37.5 grams (0.18 mole) of freshly distilled ethyl silicate and 30 ml. of ether was added dropwise with stirring to a solution of 0.45 moles of naphthyllithium (made by the indirect procedure) in 600 ml. of ether. The mixture was allowed to stir for 1/2 hour. After pouring in 300 ml. of water, separating the layers, and reducing the volume by evaporation, the solution was set aside to crystallize. White crystals formed overnight and were collected and recrystallized from petroleum ether. The yield of pure di-1-naphthyl di ethoxysilane was 80% of theoretical and it melted at 100-101°C.

## Observations

The melting points found for each compound along with published melting points are shown in Table I. Agreement with published melting points exists in most cases.

Tri phenyl-2-naphthylsilane was found by this author to exhibit the property of polymorphism. Certain solids, when crystallized from solutions, can form various crystal structures depending on the rate of cooling. These different structures can melt at different melting points. This property is known as polymorphism.

The elemental analysis of the compounds was done by Huffman Micro Analytical Laboratories and the results of the analysis are shown in Table II. The compound trimethyl-1-naphthyl silane is the only compound that is in error in silicon content. However, this author believes that this is due to impurities in the compound which were known to be present.

It was found in all cases that the indirect procedure for preparing 1- or 2-naphthyllithium gave the cleanest final product in the largest yields.

An attempt to synthesize three additional compounds was made. These compounds are tri-1-naphthyl phenylsilane, tri-2-naphthyl phenylsilane, and tri-2-naphthyl chlorosilane.

The attempted synthesis of tri-2-naphthyl chlorosilane involved the same procedures used in the synthesis of tri-1-naphthyl chlorosilane. The reactants were 2-naphthyllithium and silicon tetrachloride. The product from this reaction melted at 185-186°C and the absorption spectrum of the product closely resembled the absorption spectrum of 2-2'-binaphthyl. The elemental analysis showed 99% carbon and hydrogen content.

The attempted synthesis of tri-2-naphthyl phenyl silane was done in two steps. The first step was to make phenyl trifluorosilane from phenyl trichlorosilane. The second step was to react the fluoride with 2-naphthyllithium. The final product melted at 185-186°C and the absorption curve resembled the absorption curve of 2-2'-binaphthyl. The elemental analysis of this product also showed a 99% content of carbon and hydrogen.

The compound 2-2'-binaphthyl melts at 187-188°C (Ref 11). This fact and the above data indicates the by-product 2-2'-binaphthyl was isolated in the attempted synthesis of the tri-2-naphthylsilanes.

The synthesis of tri-1-naphthyl phenylsilane was attempted three times. Each attempt involved different synthesis steps. However, each final product showed a lower carbon content than expected in the elemental analysis. Although the evidence is not conclusive, it appears as if the compound di-1-naphthyl phenyl chlorosilane was made each time.

## Table I

## Physical Properties of the Naphthylsilanes

| Silane Compound | Melting Point |  | Glass-Forming |
|---|---|---|---|
|  | Observed ($^oC$) | Literature ($^oC$) |  |
| Triphenyl-1-naphthyl | 176-177 | 172-173 (a) | Yes |
| Diphenyl di-1-naphthyl | 194-195 | 194-195 (a) | Yes |
| Tri-1-naphthyl chloro | 210-211 | 210-211 (a) | Yes |
| Di-1-naphthyl diethoxy | 100-101 | 100-101 (a) | No |
| Di-1-naphthyl phenylethoxy | 163-164 | ----- (c) | Yes |
| Trimethyl-1-naphthyl | ----- (d) | ----- (d) | No |
| Triphenyl-2-naphthyl | 126-143 | 145-147 (b) | Yes |
| Diphenyl di-2-naphthyl | 162-163 | ----- (c) | Yes |

(a) Ref 9:4640-4644
(b) Ref 8:5933-5936
(c) Not found in literature
(d) A liquid boiling at 103$^oC$ at 2.5 mm Hg.

## Table II

**Elemental** Analysis
(in percent by weight)

| Silane Compound | Carbon |  | Hydrogen |  | Silicon |  |
|---|---|---|---|---|---|---|
|  | Cal (a) | Obt (b) | Cal (a) | Obt (b) | Cal (a) | Obt (b) |
| Triphenyl-1-naphthyl | 87.0 | 86.87 | 5.7 | 5.7 | 7.26 | 7.2 |
| Diphenyl di-1-naphthyl | 88.2 | 88.0 | 5.5 | 5.4 | 6.42 | 6.7 |
| Tri-1-naphthyl chloro | 81.0 | 79.85 | 4.73 | 4.97 | 6.3 | 6.05 |
| Di-1-naphthyl diethoxy | 77.4 | 77.3 | 6.45 | 6.5 | 7.54 | 7.6 |
| Di-1-naphthyl phenylethoxy | 83.1 | 83.25 | 5.9 | 5.72 | 6.9 | 6.5 |
| Trimethyl-1-naphthyl | 78.0 | 78.15 | 8.0 | 7.9 | 14.0 | 10.9 |
| Triphenyl-2-naphthyl | 87.0 | 87.1 | 5.7 | 5.7 | 7.26 | 7.2 |
| Diphenyl di-2-naphthyl | 88.2 | 88.2 | 5.5 | 5.64 | 6.42 | 6.55 |

(a) Calculated
(b) Obtained

# IV. Experimental

## Equipment

Absorption. In this study, the instrument used was a Cary Recording Spectrophotometer Model 11MS. This instrument, designed by H. H. Cary (Ref 5:558), consists of a hydrogen tube and incandescent lamp sources, a double monochromator with two 30 quartz prisms, and optics for splitting the incident light into "reference beam" and "sample beam" which are focused on separate photomultiplier tubes. The ratio of the two photoelectric currents is amplified and recorded directly in absorbance (optical density E). An electrical cam provides recording linearly in wavelength so that the instrument produces a finished spectrum at a tremendous saving of time. The absorbance range, 0.0 to 2.5, is conveniently large, but with some sacrifice of accuracy can be changed to 1.0 to 3.5 by means of a switch.

The usable wavelength range extends from 2100 Å to 6000 or 8000 Å, depending on the response of the particular phototubes. A set of potentiometers covering this entire range is provided to compensate for any mismatching of cells. Thus, any necessary corrections of absorbance values due to mismatching may be made electrically.

Fluorescence and Phosphorescence. An Aminco-Keirs Spectrophosphorimeter was used in the experiments involving fluorescence, phosphorescence, and decay times. This instrument is essentially a double monochromator device using a xenon light source and photomultiplier detectors. With a simple adjustment the instrument can be used as a phosphorimeter or a fluorometer.

The spectrophosphorimeter consists of an optical unit, power supply, photomultiplier, microphotometer, and accessary equipment. Figure 2 is a functional drawing of the instrument and will be used in the following discussion.

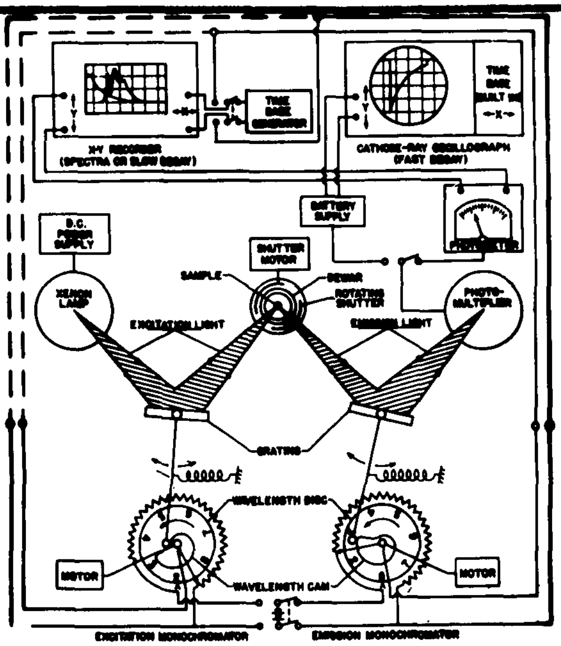


Fig. 2

Spectrophosphorimeter
Functional Drawing

(Ref 2:4)

The difference in recording fluorescence rather than phosphorescence is shown in Figure 3. A different cell compartment, slit widths, rotating shutter, and a cooling device are the necessary modifications for studying phosphorescence.

In all cases the principles of operation are the same. Light from the xenon lamp is dispersed by the excitation monochromator (grating type) into monochromatic radiation. A series of slits determine the spectral bandwidth of light reaching the sample. The light from the sample passes through another series of slits and is dispersed by

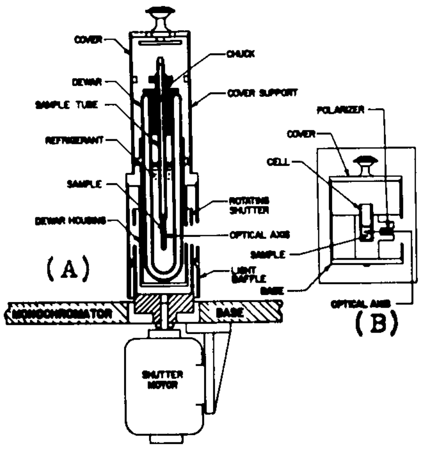


Fig. 3

Spectrophosphorimeter Modifications
(A) Phosphorescence
(B) Fluorescence

(Ref 2:11)

a similar monochromator in monochromatic radiation which falls on the photomultiplier. The signal from the photomultiplier is fed into a photometer where it is amplified. Photometer output is coupled to the x-y recorder for spectra recording and is simultaneously indicated by a self-contained meter on the photomultiplier. The rotating shutter is driven by a variable speed motor when measuring phosphorescence. The rotating shutter permits the observation of phosphorescence without the presence of fluorescence.

The gratings are oscillated by motor-driven cams to which are coupled graduated discs for visual observation and adjustment of the wavelength. Potentiometers, coupled to the gratings, supply wavelength information to the horizontal axis of the x-y recorder. When the sweep power is connected to the scanning emission monochromator, and the excitation monochromator is set at a wavelength for maximum activation, a wavelength versus intensity diagram (phosphorescence spectrum) is plotted. Similarly, when the sweep power is connected to the scanning excitation monochromator, and the emission monochromator is set at a wavelength for maximum emission, a wavelength versus intensity diagram (phosphorescence activation spectrum) is plotted.

When the x-axis of the x-y recorder is driven by an internal time base generator and the y-axis coupled to the photometer output (with both monochromators set for maximum emission), an intensity versus time diagram (phosphorescence decay curve) can be plotted. The sample is opened to the activating light until the emission reaches its maximum value, whereupon the x-axis of the recorder is started. A slit between the light source and sample is then closed, and the recorder plots the ensuing decay. For shorter mean lifetimes ($<0.5$ second) an oscilloscope must be used instead of a recorder; however, the lifetimes determined in this study were, in all cases, sufficiently long to permit use of the time base recorder.

The manufacturer of the Spectrophosphorimeter recommends the use of either the 1P21 or 1P28 phototubes. A 1P21 tube was chosen for this study because of its flatter response in the 350 to 600 millimicron range.

Calibration of the monochromators and x-y recorder was checked with a pen-ray quartz lamp which emits the lines of the mercury spectrum. The emission monochromator was calibrated over its full range with these lines, after which the excitation monochromator calibration was verified by use of an aluminum foil reflector in the sample cell. The reflected light was dispersed by the calibrated emission monochromator and detected by the photomultiplier. A maximum reading on the photometer was taken as the point at which the wavelengths of the two monochromators coincided. The x-axis of the recorder was calibrated against the emission monochromator. In this manner, the monochromators and recorder were calibrated.

Any correction for the relative intensities of emission peaks for a compound can be made by the comparison of the experimentally obtained fluorescence spectra of naphthalene with the spectra of naphthalene found in Appendix D. Relative intensity corrections for phosphorescence can be made by the comparison of the experimentally obtained spectra of indole with the spectra of indole found in Appendix D.

## Experimental Procedure

Absorption. After purifying the sample of compound, 100 mg. of the sample was carefully weighed on an analytical balance. The material was then placed in a 100 ml. volumetric flask. In this flask, 100 ml. of cyclohexane was added. This made a dilute solution of 1 mg./ml.. A spectrum of cyclohexane as the reference solution and cyclohexane as the sample was obtained in order to zero the optical density readings. The cell width was 1.0 cm. in thickness. The absorption spectrum of the sample was then obtained with cyclohexane as the reference solution.

In most cases, a concentration of 1 mg./ml. was too high to obtain the complete spectrum. Therefore, after the first spectrum was obtained, a new concentration was calculated that would give a peak absorption in the range of 1.0 to 2.0 optical density. The necessary dilution was then made and a new spectrum was obtained.

The cells used were cleaned with acetone and dried after each determination of spectrum. Also, these blank cells were placed in the Cary and a spectrum was obtained in order to see if any sample remained in the cells.

Fluorescence in Cyclohexane at 298°K. The dilute solutions of each compound made for the absorption studies was used for this experiment. The fluorescent attachment used is shown in Figure 3. The cell was approximately 1.0 cm. in diameter and 4.0 cm. in height. A fluorescence spectrum of each compound was obtained at maximum excitation and a activation spectra was obtained at maximum emission.

Fluorescence as a Glass. A new technique was developed by this author for studying fluorescence of glass forming compounds.

It was shown by Polk (Ref 15:68) that maximum emission occurs when the sample is at an angle of 45° to the incident light. The cell holder for the cells used in the fluorescences studies is square shaped, and a flat object can be placed in the cell holder diagonally. Figure 4 shows the graphite holder made for this purpose. The sample is melted and cooled to form a glass in the indentation shown in Figure 4.

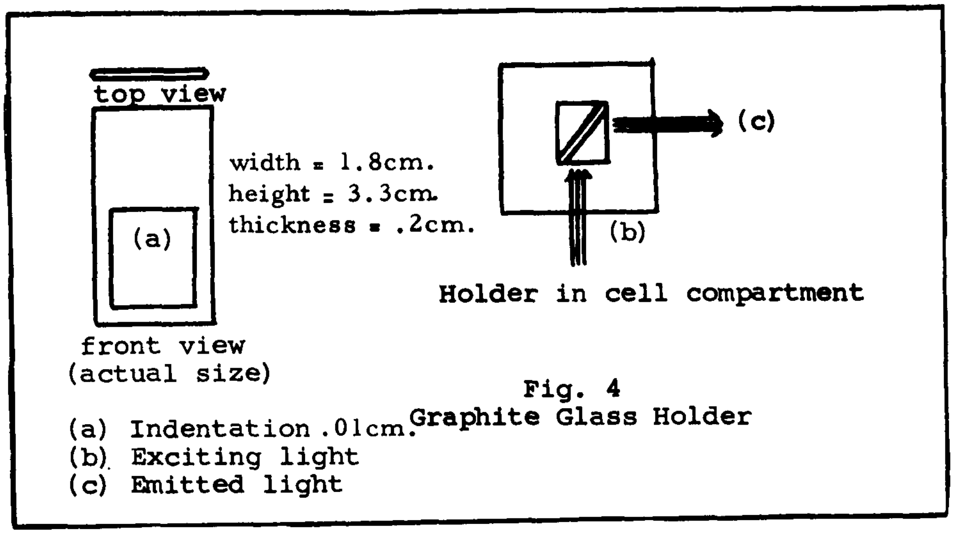


Fig. 4
Graphite Glass Holder

Graphite was used since it showed no appreciable fluorescences at all wavelengths. The emitted light is surface fluorescence and self-absorption is minimized. The fluorescence spectra of each compound which formed a glass was obtained at 298°K along with the excitation spectra at maximum emission.

Fluorescence in EPA at 298°K and 77°K. EPA is a mixture consisting of five parts ethyl ether, five parts isopentane, and two parts ethyl alcohol. The EPA which was used in these experiments was prepared under carefully controlled conditions by the American Instrument Company of Silver Spring, Maryland.

EPA forms a rigid transparent glass at liquid air and liquid nitrogen temperatures and therefore can be used in the study of phosphorescence. However, in this experiment the rotating shutter was removed in the Spectrophosphorimeter so that fluorescence could be observed.

The procedure which follows was strictly adhered to in making up solutions of the silanes for investigations of fluorescence in EPA. A 10 milligram sample of each compound was weighed and placed in a tightly-stoppered glass vial. About twenty-five milliliters of EPA were poured into a small beaker, and a previously cleaned pipette was rinsed with about ten milliliters of the solvent. Ten milliliters of EPA were then pipetted into the vial containing the sample; the vial was tightly stoppered and placed in a dark drawer until the solution was used, which was always within ten minutes of preparation. EPA, if left exposed to the air, would form impurities. The freshly-mixed solution was transferred to the spectrophosphorimeter sample tube (see Figure 3) via a clean hypodermic syringe. Before use, the syringe and needle were rinsed twice with acetone, dried, and rinsed twice with EPA. About 1/2 milliliter of the solution was then used to rinse the syringe and needle, after which an additional 1/2 milliliter was measured into the syringe and injected into the sample tube. The sample tube was stoppered with a small plug of cotton.

The emission and activation spectra of the compound were obtained at room temperature after which liquid nitrogen was poured into the Dewar flask. The emission and activation spectra of the compound was then obtained at liquid nitrogen temperature. The Dewar flask was washed after each use with shampoo to prevent dust particles from causing bubbles to form.

Phosphorescence and Decay Curves. The rotating shutter was placed in the spectrophosphorimeter and the same procedure for studying fluorescence at 77°K was used to obtain the phosphorescence spectra of the silanes at 77°K in EPA.

Decay curves were obtained by setting the monochromators at maximum emission and excitation and with the recorder on time base, a mask slit was inserted in front of the exciting light. Thus, a decay curve of the phosphorescent light was obtained.

# V. Results

The results in the following pages show many important characteristics of the naphthyl silanes. These characteristics were obtained from luminescence data. Certain aspects of this data must be explained. These aspects are the intensities of emission bands and accuracies of extinction coefficients.

The relative intensities of the fluorescence of the silanes could not be reproduced with the experimental arrangement. The reason that the intensities could not be accurately reproduced was the extreme sensitivity of the detected emission intensities to geometrical placement of the sample in the cell. The emission intensities which can be meaningfully compared are the relative intensities of two or more bands in the same spectrum of a specific sample at a single temperature.

The absorption spectrum contained in the results for any one compound was not accepted as correct until three successive spectra agreed to the tenth place for the molecular extinction coefficient at all wavelengths.

## Absorption Spectra Shifts in Wavelength

Figure 5 graphically represents the absorption spectra obtained for six compounds. It is apparent that the mononaphthylsilanes behave much the same way in absorbing light as other mononaphthyl compounds.

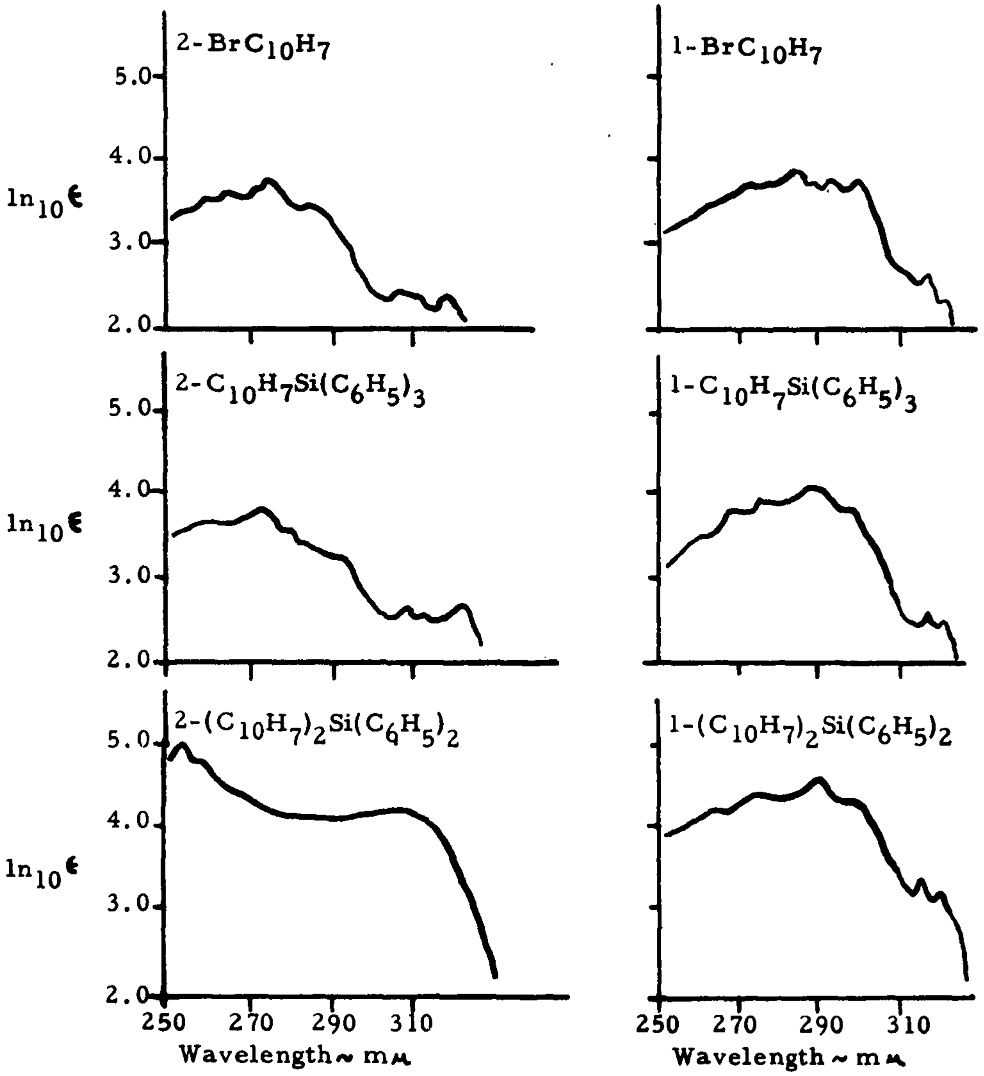


Fig. 5

**Absorption Spectrum Changes Due to Position and Number of Naphthalene Molecules**
(In cyclohexane at 298°K)

Figure 5 shows the spectra of 1- and 2-bromonaphthalene. However, spectra of other mononaphthalenes are similar to those of bromonaphthalene. The absorption curve for di-1-naphthyl diphenylsilane is similar to the absorption curve for the 1-mononaphthylsilane, with only an increase in extinction coefficient at corresponding wavelengths. A significant difference is noted in the absorption curve for di-2-naphthyl diphenylsilane.

## Extinction Coefficient Correlation with Number of Molecules

1-Naphthylsilanes. As shown in Table III, the molecular extinction coefficients were calculated for the 1-naphthylsilanes at the wavelength for maximum absorbance. The absorbance of the 1-naphthyl phenylsilanes was found to depend on the number of naphthalene molecules attached to the silicon atom. The ethoxy and methyl naphthylsilanes did not show this same property.

2-Naphthylsilanes. The molecular extinction coefficients at the wavelength for maximum absorbance were also calculated for the 2-naphthylsilanes. No one to one ratio in extinction coefficients for the 2-naphthyl groups exists (see Table III).

## Emission Characteristics of Naphthyl Phenylsilanes

1-Naphthyl Phenylsilanes. Fluorescence emission spectra are shown in Figure 6, and it is apparent that the emission characteristics of the 1-naphthyl phenylsilanes are unaltered when one or two naphthalene

## Table III

### Absorption Properties of Naphthylsilanes
(in cyclohexane at 298°K)

| Silane Compound | Wavelength of Maximum Absorption ($m\mu$) | Molecular Extinction Coefficient ($\epsilon$) |
|---|---|---|
| Triphenyl-1-naphthyl | 288 | $1.0X10^4$ |
| Diphenyl di-1-naphthyl | 288 | $2.0X10^4$ |
| Tri-1-naphthyl chloro | 290 | $3.0X10^4$ |
| Di-1-naphthyl diethoxy | 286 | $1.5X10^4$ |
| Di-1-naphthyl phenylethoxy | 288 | $1.8X10^4$ |
| Trimethyl-1-naphthyl | 283 | $8.2X10^3$ |
| Triphenyl-2-naphthyl | 272 | $6.3X10^3$ |
| Diphenyl di-2-naphthyl | 254 | $6.8X10^4$ |
| Naphthalene | 275 | $5.6X10^3$ |

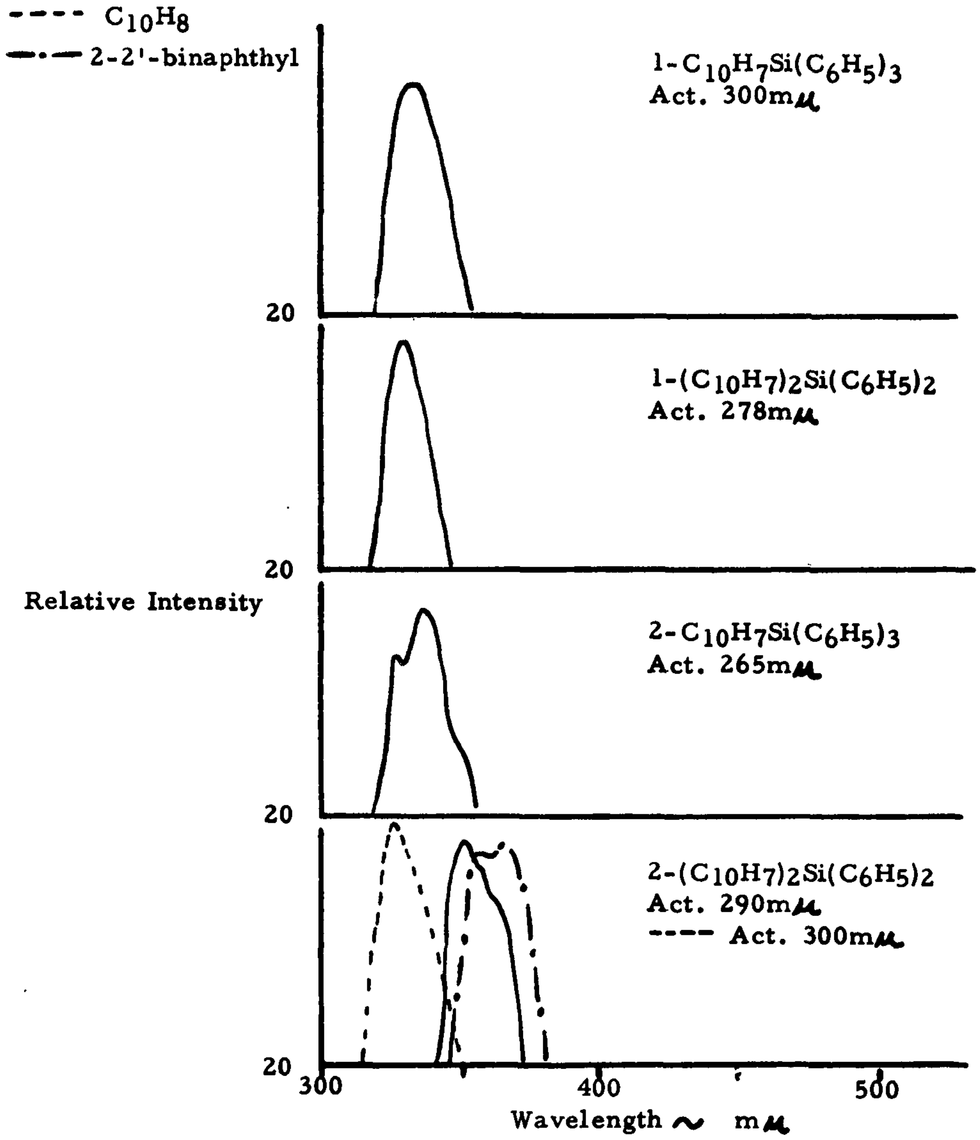


Fig. 6

Fluorescence Emission Spectra of Naphthyl Phenylsilanes
(In cyclohexane at 298°K)

molecules are attached to the silicon atom. It is also noted that the emission bands correspond to the same wavelength of emission for a single naphthalene molecule.

2-Naphthyl Phenylsilanes. As shown in Figure 6, the fluorescence emission characteristics of the 2-naphthyl phenylsilanes are different when one or two naphthalene molecules are attached to the silicon atom. The emission bands shift to longer wavelengths as the number of naphthalene molecules increase. It is also noted that there exists a similarity of spectra between di-2-naphthyl diphenylsilane and 2-2'-binaphthyl.

## Fluorescence Emission Changes for Glass Emission

It was experimentally observed that the emission spectra of the glassy naphthylsilanes were quite different than the emission spectra of the naphthylsilanes in solution. This difference is shown graphically in Figure 7 for the mononaphthylsilanes. In particular, it is noted that the glass emission spectra is at longer wavelengths in all cases. This same property was observed for all the glass-forming silanes (see appendices).

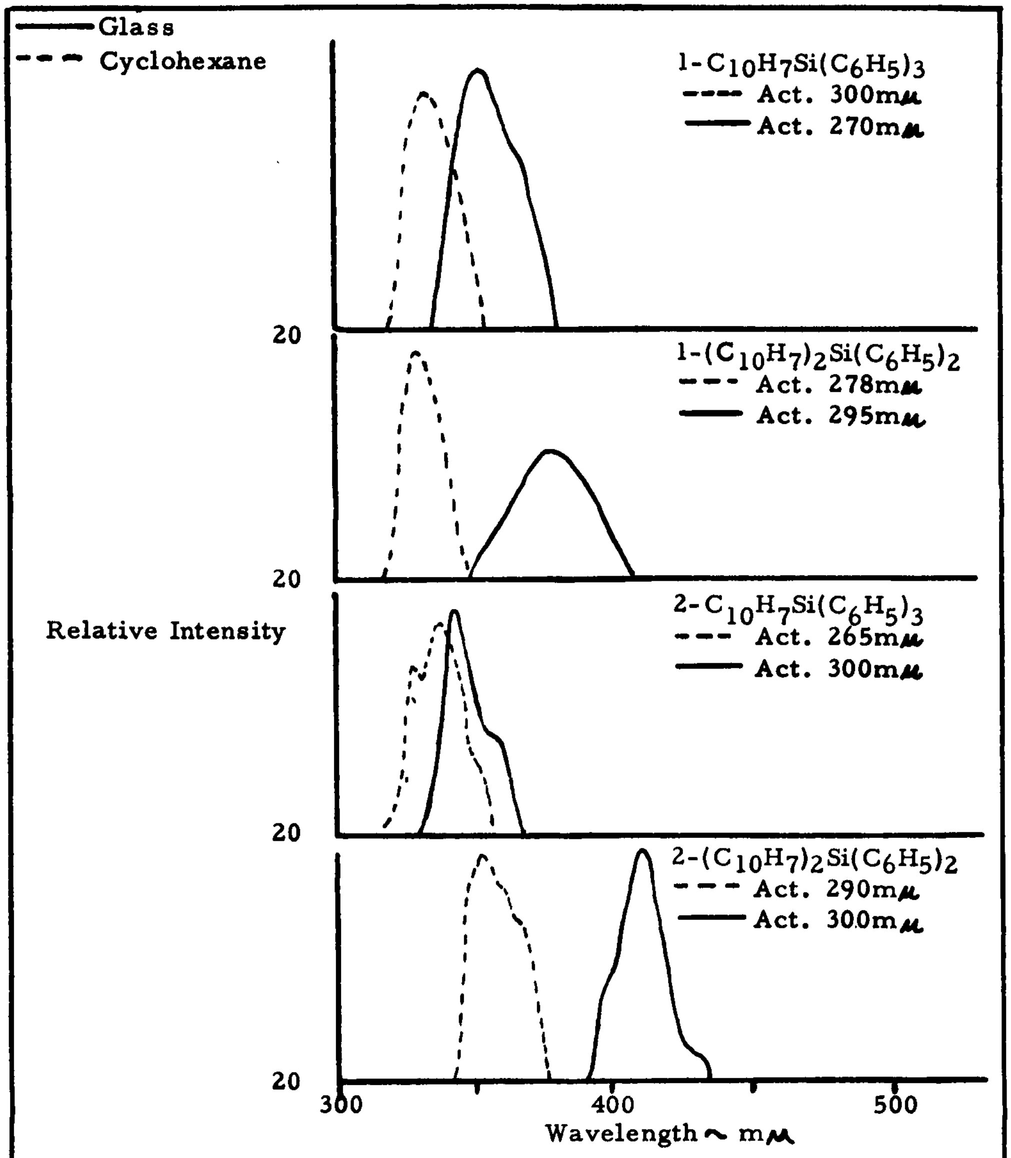


Fig. 7

Fluorescence Emission Spectra of Naphthyl Phenylsilanes - Comparing Glass Emission Spectra with Emission Spectra in Cyclohexane (at 298°K)

## The Emission for Groups Other Than Naphthalene

It was experimentally observed that no substituent group attached to the silicon atom affected the emission properties of the naphthalene molecule in the 1-naphthylsilanes (see Figure 8). Compounds were not made which could show a substituent group effect in the 2-naphthylsilanes.

## Solvent Effects

The most intense fluorescence emission band for the 1- and 2-naphthyl phenylsilanes was not significantly changed in wavelength when the solvent was changed. This can be seen in Figure 9. However, there are differences in the number of emission bands in some cases. It is common, in most solvents whose molecules are polarized, to find fluorescence emission characteristics altered by the effect of the polarization of the solvent. Since EPA contains molecules that are slightly polarized, emission characteristics in EPA should be slightly different than the emission characteristics of a compound in any other solvent.

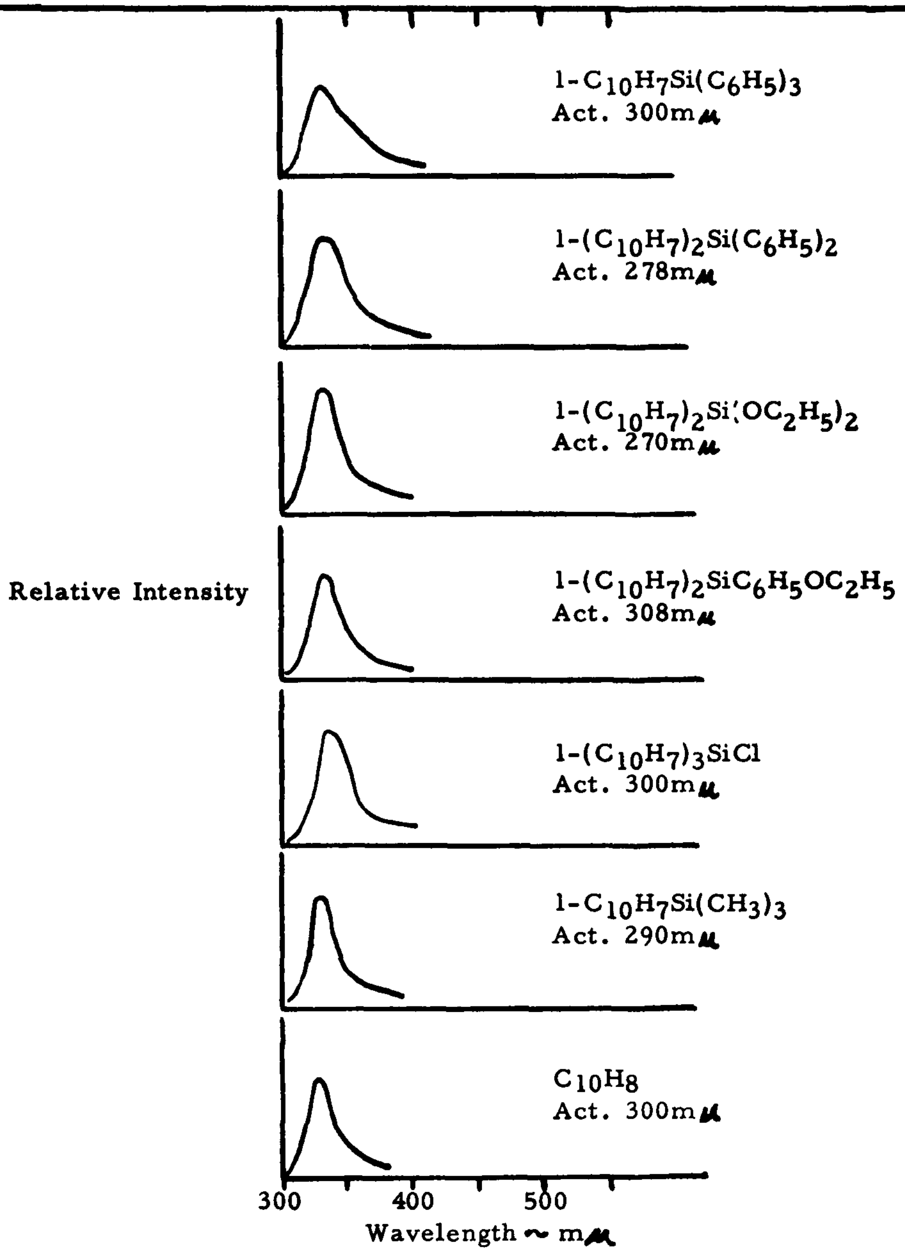


Fig. 8

Fluorescence Emission Spectra of the Naphthylsilanes
(In cyclohexane at 298°K)

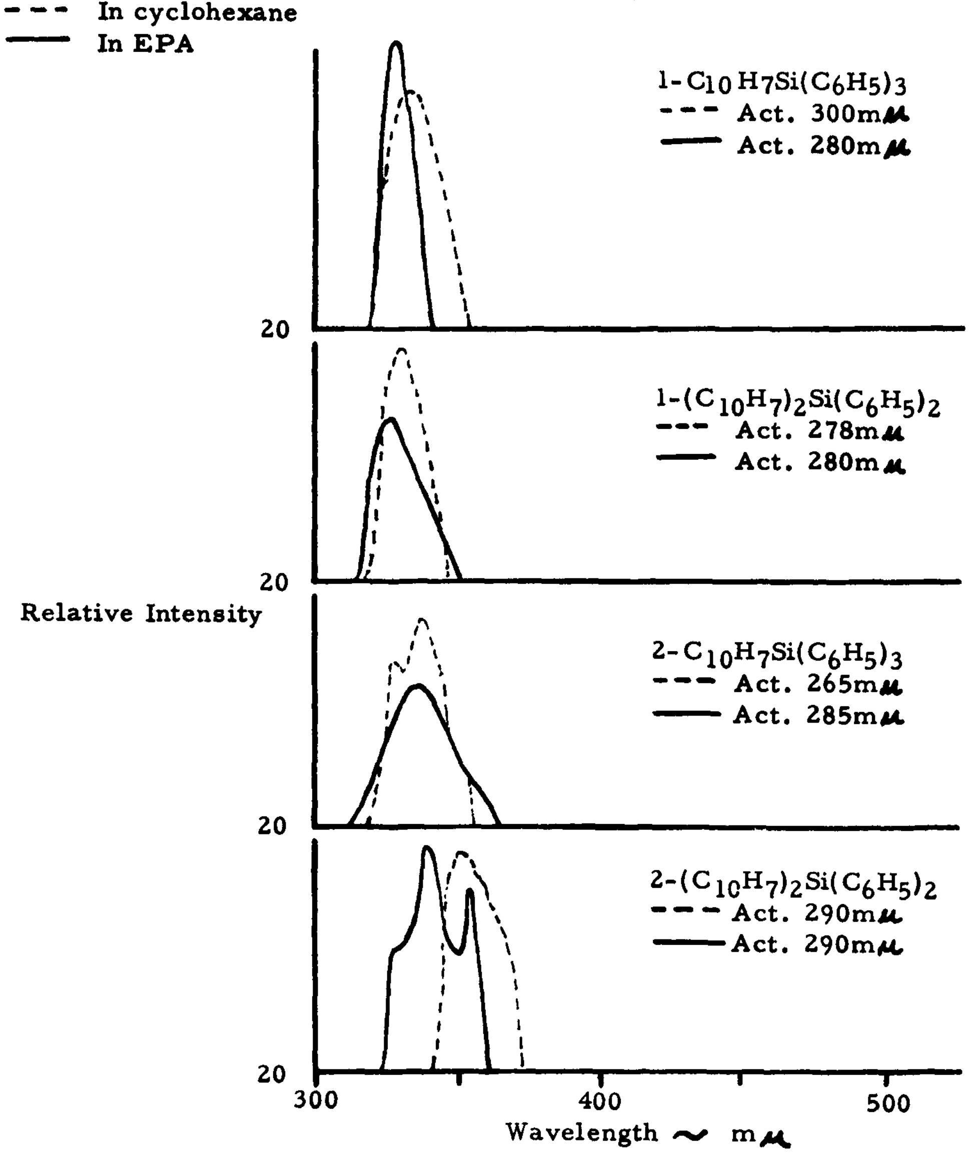


Fig. 9

Fluorescence Emission Solvent Effects
(at 298°K)

### Temperature Effects

The temperature effects on the fluorescence emission spectra of the naphthyl phenylsilanes are shown in Figure 10. Sharper spectral structure was observed at 77°K and emission bands not distinguishable at 298°K were observed at 77°K.

### Phosphorescence Results

The phosphorescence results are summarized on Table IV. It is noted that the maximum phosphorescence emission band for each compound is similar to the emission band for naphthalene. The differences are most likely caused by perturbations from the substituent groups around the silicon atom.

### Mean Phosphorescent Lifetimes

Mean phosphorescent lifetimes for each compound were calculated from the decay curves as follows. It was assumed that the lifetime of a phosphorescence band could be represented by the formula

$$I = I_O e^{-t/\tau}$$

where $I$ = Intensity of emitted light at any time $t$

$I_O$ = Intensity of emitted light at time $t = O$

$e$ = Base of natural logrithums

$\tau$ = Mean lifetime in seconds

$t$ = Time in seconds.

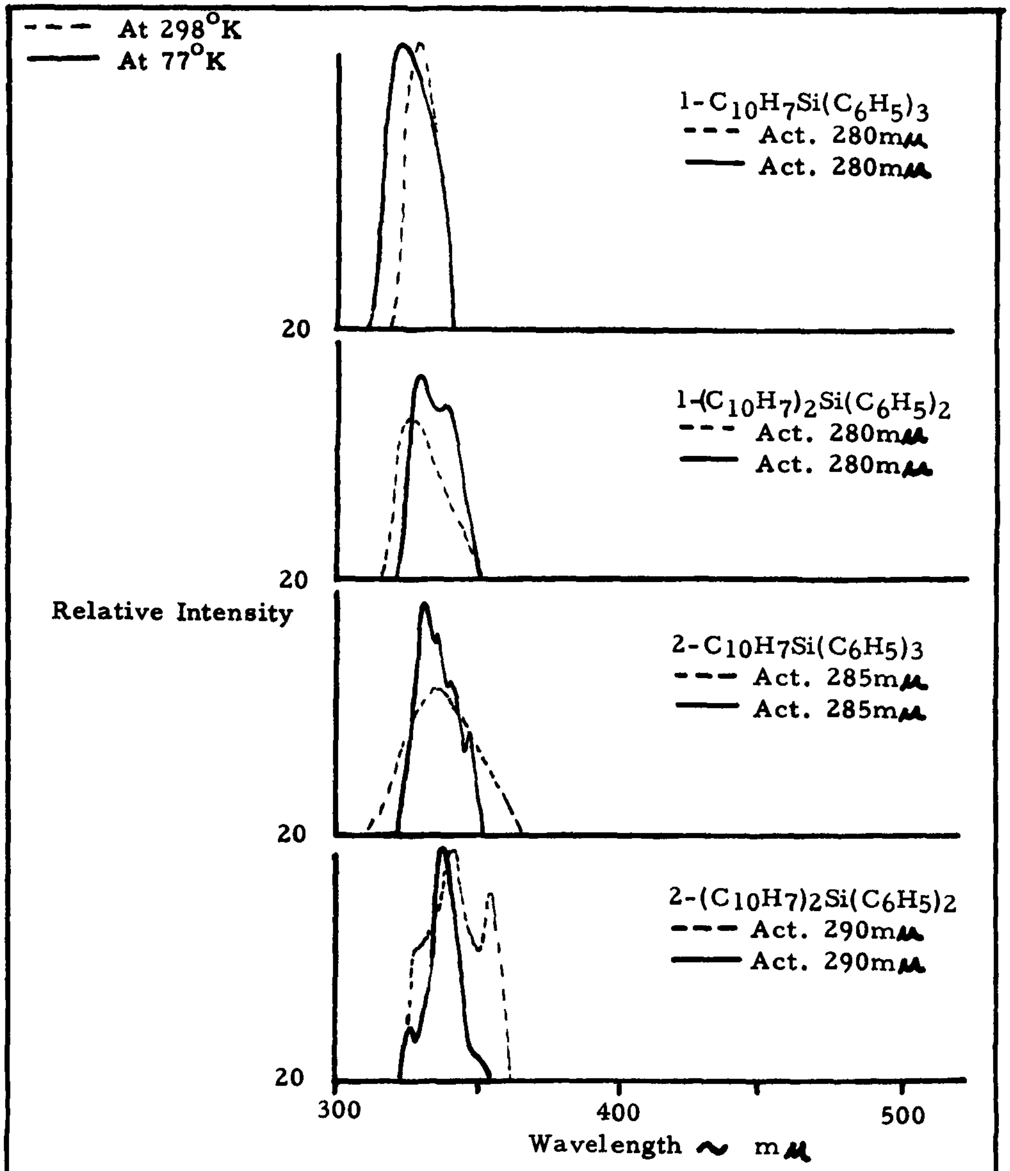


Fig. 10

Fluorescence Emission Temperature Effects
(In EPA)

## Table IV

Phosphorescence Properties of Naphthylsilanes
(in EPA at $77^{o}K$)

| Silane Compound | Wavelength of Maximum Emission ($m\mu$) | Activation Band for Maximum Emission ($m\mu$) | Mean Lifetime (sec.) |
|---|---|---|---|
| Triphenyl-1-naphthyl | 500 | 315 | 2.95±.02 |
| Diphenyl di-1-naphthyl | 505 | 330 | 2.71±.03 |
| Tri-1-naphthyl chloro | 510 | 320 | 1.80±.04 |
| Di-1-naphthyl diethoxy | 510 | 320 | 2.10±.01 |
| Di-1-naphthyl phenylethoxy | 505 | 320 | 2.71±.02 |
| Trimethyl-1-naphthyl | 510 | 318 | 2.10±.03 |
| Triphenyl-2-naphthyl | 510 | 315 | 2.25±.02 |
| Diphenyl di-2-naphthyl | 500 | 323 | 2.71±.03 |
| Naphthalene | 500 | 315 | ----- (a) |

(a) Not obtained

If ln I is plotted against time, the slope of the line is $\tau$ The average value of $\tau$ was obtained from replicate plots of a compound's decay curves (see Appendix E).

The results of the mean phosphorescent lifetimes are shown in Table III. The precision of the mean phosphorescent lifetimes shown in Table III is the average deviation from the mean of five independent determinations.

## VI. Discussion and Conclusions

The results in the preceding pages show the experimental data obtained on each compound. These results indicate important characteristics of the compounds used in this study and warrant further discussion.

### Absorption

The 1-naphthyl phenyl series showed the property of independent absorption of the naphthyl groups. There is indicated that no energy transfer occurs between the naphthalene molecules. The naphthalene molecules attached to the silicon atom act as if they were absorbing and emitting light as single naphthalene molecules.

The 2-naphthyl phenyl compounds do not show the property of independent absorption by the naphthalene molecules. The results indicate that when two molecules of naphthalene are attached to the silicon atom with the silicon in the two position, there is energy transfer within the molecule. Figure 11 shows the experimentally obtained absorption curve of 2-2'-binaphthyl (Ref 1). The similarity of these two curves indicates that the silicon atom acts as a bridge for intermolecular energy transfer in di-2-naphthyl diphenylsilane.

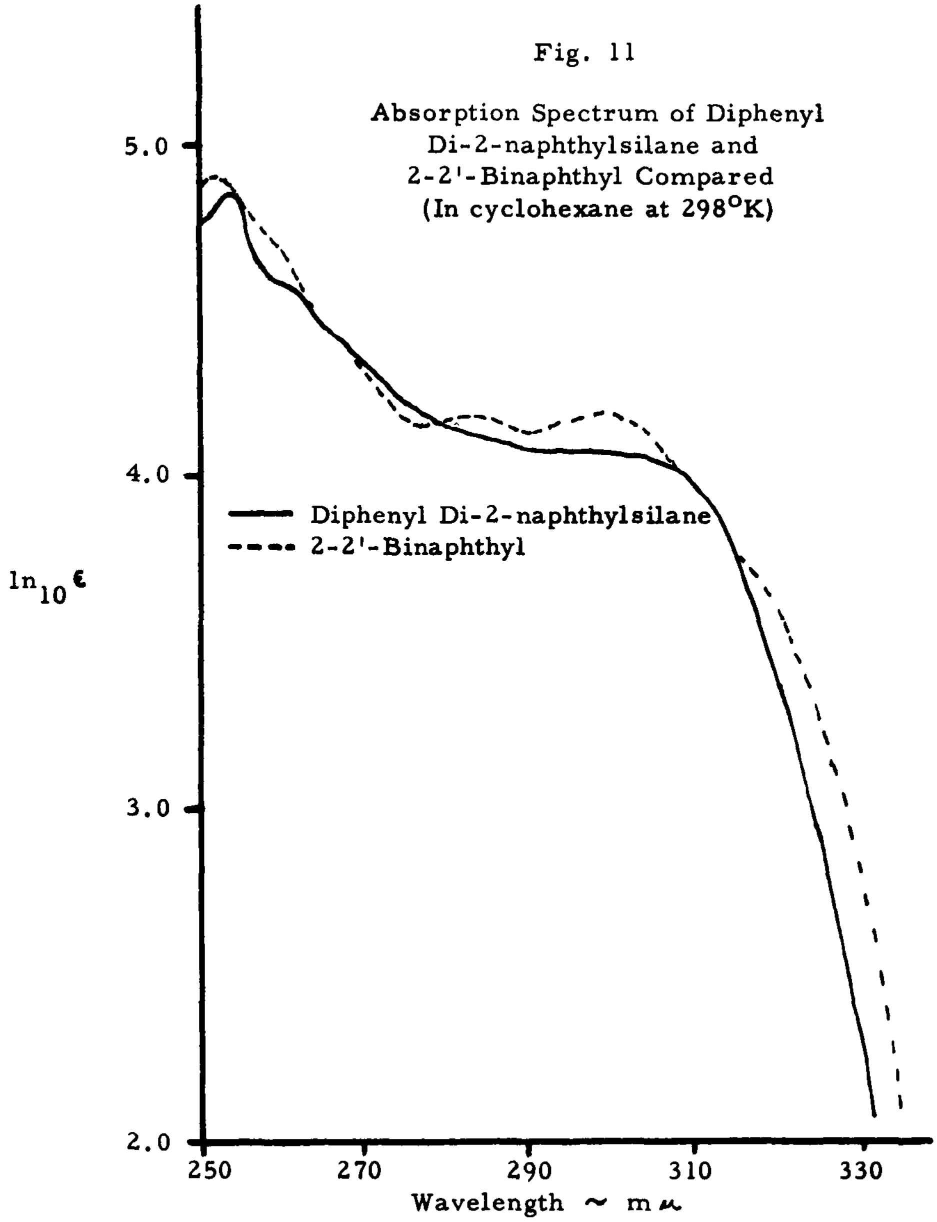


Fig. 11

Absorption Spectrum of Diphenyl Di-2-naphthylsilane and 2-2'-Binaphthyl Compared (In cyclohexane at 298°K)

Since the fluorescence spectra of the glass-forming silanes as glasses were shown to be different than the spectra obtained of the compounds in solution, the absorption curve for triphenyl-1-naphthylsilane was obtained with this compound as a glass, and is shown in Figure 12. This absorption curve is very different from any curves obtained of this compound in solution. No fine structure was obtained and the absorption extends into the visible region. No explanation of this characteristic can be presented at this time due to the lack of pertinent information.

## Fluorescence

If the emission bands of the 1-naphthylsilanes are compared with the emission bands of naphthalene, it is apparent that the 1-naphthylsilane compounds emit light from each naphthyl molecule independent of other groups on the silicon atom. No correlation of this independent emission is observed for the 2-naphthylsilane compounds. It is thought, therefore, that the silicon atom on the two position of naphthalene may contribute somewhat to changing the orbital structure of the naphthalene molecule, but this change is not the major contributing factor. Rather, the major process seems to be in the interaction of the naphthalene molecules. This conclusion is drawn since triphenyl-2-naphthylsilane behaved much like naphthalene

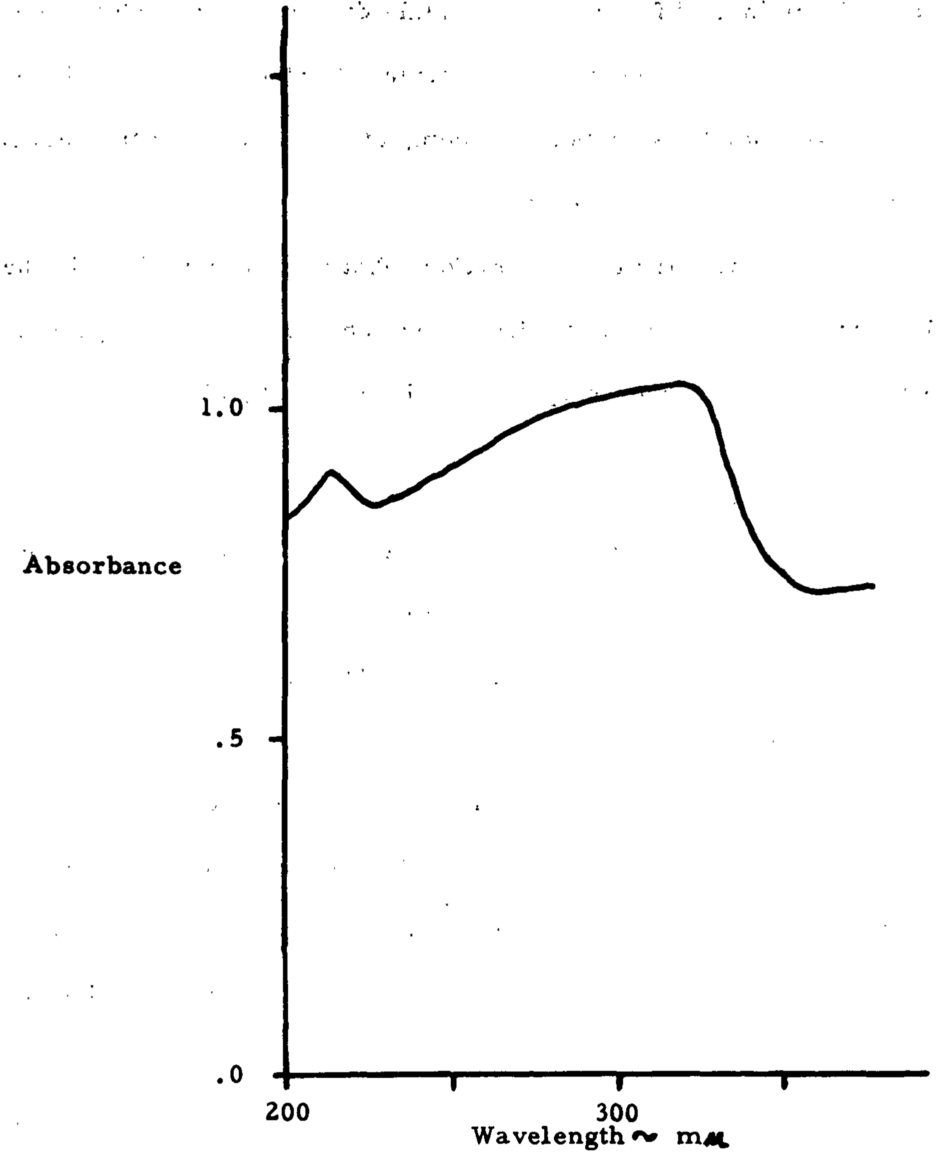


Fig. 12

Absorption Spectrum of Triphenyl-1-naphthylsilane
(as a Glass at 298°K)

but with the loss of fine structure; while diphenyl di-2-naphthylsilane did not emit like a naphthalene molecule. Further work must be done on the 2-naphthylsilanes before a complete explanation of the energy transfer process can be presented.

There appears to be no major substituent group effect in the 1-naphthylsilanes. That is, the phenyl, chloro, and ethoxy groups do not alter the fluorescence spectra of the 1-naphthylsilanes.

## Phosphorescence

In most cases, the activation maximum for phosphorescence at 77°K in EPA occurred at the same wavelength as that for activation of fluorescence at the same conditions. This demonstrates singlet-triplet interconversion.

The phosphorescence of all the compounds were in the 500 millimicron region and no significant differences were noted for any of the compounds. The mean lifetimes of all the compounds were comparable to previous glass-forming silanes. However, triphenyl-1-naphthylsilane and diphenyl di-1-naphthylsilane did show short-lived phosphorescence as a glass at room temperature. This quality should be investigated further.

Comparison of phosphorescence data indicates that the phosphorescence observed for each compound is that of the naphthalene molecule with perturbations caused by the groups around the central silicon atom.

It was also found that in the 1-naphthyl compounds, the phosphorescence was excited at the wavelength comparable to the last distinguishable peak in the absorption spectra.

## Summary

Synthesis. The indirect method (metal halogen interchange) is the first step in a simple synthesis scheme used in this study to prepare 1- or 2-naphthylsilanes. The yields are good (up to 80%), and the compounds all fluoresce in the visible region. A direct method of preparing 1- or 2-naphthyllithium was used, but the resulting end product was of poor quality and quantity.

Absorption. The 1-naphthyl phenylsilanes prepared in this study absorb light in discrete quantities directly related to the number of naphthalene molecules attached to the silicon atom. No apparent relationship of this kind exists for the 2-naphthyl phenylsilanes.

Fluorescence. The results of this study indicate that the 1-naphthylsilanes fluoresce at approximately the same wavelength as that of naphthalene. The 2-naphthylsilanes fluoresce at wavelengths longer than that of naphthalene. Energy transfer between naphthalene molecules is indicated in the 2-naphthylsilanes. No substituent group emission effect could be seen in the naphthylsilanes.

Phosphorescence. The phosphorescence observed for these compounds is that of the naphthalene molecule with perturbations caused by the substituent groups. Mean phosphorescent lifetimes are comparable to lifetimes of previous glass-forming silanes.

## VII. Recommendations

During the course of this investigation, many areas of research were found which could not be done. Also, areas of work needing further study were found and these recommended areas of work are presented in the following:

(1) In order to obtain information concerning the phosphorescence observed of the naphthyl silanes as a glass at 298°K, the spectrum of the glass-forming silanes as a glass should be obtained at 77°K.

(2) To further investigate the substituent effect, 1- and 2-naphthylsilane, di-1 and di-2-naphthylsilane, and tri-1 and tri-2-naphthylsilane should be synthesized and their luminescence properties obtained.

(3) The absorption data of each glass-forming silane as a glass should be obtained. This data may yield information concerning the energy levels of the silanes as a glass.

(4) The synthesis and study of the compound di-1-naphthyl di-2-naphthylsilane would yield further information pertaining to energy transfer in the naphthylsilanes.

(5) Each glass-forming silane showed many properties similar to organic scintillators used for the detection of ionizing radiation. The scintillation properties of the naphthylsilanes should be investigated.

(6) Tri-1-naphthyl phenylsilane and tri-2-naphthyl phenylsilane should be synthesized and their luminescent properties investigated. This information would add further knowledge on the behaviour of naphthylsilanes in absorbing and emitting light.

## Bibliography

1. Adams, R., E. C. Kirkpatrick. "Structure of Gossypol." The Journal of the American Chemical Society, 60:2180 (1938).

2. Aminco-Keirs Spectrophosphorimeter. Instruction Manual. Silver Spring, Maryland: American Instrument Co. Inc., 1962.

3. Becker, R. S. and M. Kasha. "Luminescence Spectroscopy of Molecules and the Photo Synthetic System", in "The Luminescence of Biological Systems." Washington, D. C.: American Association for the Advancement of Science. 1955, pp. 25-45.

4. Birks, J. B. "The Scintillation Process in Organic Systems." IRE Transactions on Nuclear Science, NS-7:2-11 (June - September 1960).

5. Cary H. H. "New Instruments." Review of Scientific Instruments, 17:558 (1946).

6. Downs, J. W. and F. L. Smith. "Organic Glass Scintillators." Nucleonics, 16:94-96 (March 1958).

7. Gillam, A. E. Electronic Absorption Spectroscopy. London: Edward Arnold Publishers LTD., 1954, p.6.

8. Gilman, H. "Some Reactions of Silyllithium Compounds with Ethers." Journal of the American Chemical Society, 80:5933-5936 (1958).

9. Gilman, H. and C. G. Brannen. "Some 1-naphthylsilicon Compounds." Journal of the American Chemical Society, 73:4640-4644 (October 1951).

10. Heller, A. "Computation of Efficiencies of Organic Liquid Scintillators." IRE Transactions on Nuclear Science, NS-9:25 (June 1962).

11. Hystajarin, D. A. Dictionary of Organic Compounds. New York: Oxford University Press, 1953.

12. Kasha, M. "Phosphorescence and The Role of the Triplet State in the Electronic Excitation of Complex Molecules." Chemical Reviews, 41:401 (1947).

13. Lothian, G. F. Absorption Spectrophotometry. London: Hilger and Watts LTD., 1949, p.9.

14. Parker, C. A., W. I. Rees. "Fluorescence Spectrometry." The Journal of the Society of Analytical Chemistry, 103 (1962).

15. Polk, A. V. A Study of Some Basic Luminescent Properties of Five Related Tetraaryl Silanes Under Ultra-Violet Excitation. Thesis. Wright-Patterson AFB, Ohio: United States Air Force Institute of Technology, 1962.

16. Price, W. J. Nuclear Radiation Detection. New York: McGraw-Hill Book Co. Inc., 1958, p.168.

17. Sangster, R. C. and J. W. Irvine, Jr. "Study of Organic Scintillators." Journal of Chemical Physics, 24:670-715 (April 1956).

18. Spialter, L., C. W. Harris, and D. C. Priest. "The Mixed Phenyl- and p-biphenylyl-Substituted Silanes." The Journal of the American Chemical Society, 77:6227-6231 (December 1955).

19. Spialter, L.,L. Towers, and C. W. Newing. Unpublished Work, Aeronautical Research Laboratory: Wright-Patterson AFB, Ohio: (1962).

20. Weis, C. G. Some Luminescent Properties of the Mixed Phenyl- and p-biphenylyl-Substituted Silanes. Thesis. Wright-Patterson AFB, Ohio: United States Air Force Institute of Technology, 1961.

21. Weis, C. G., G. John, A. F. Vetter, and L. Spialter. "Organosilicon Compounds for Radiation Detection." Transactions of the American Nuclear Society, 4:23-24 (June 1961).

# Appendix A

## Absorption Spectra of Naphthyl Silanes

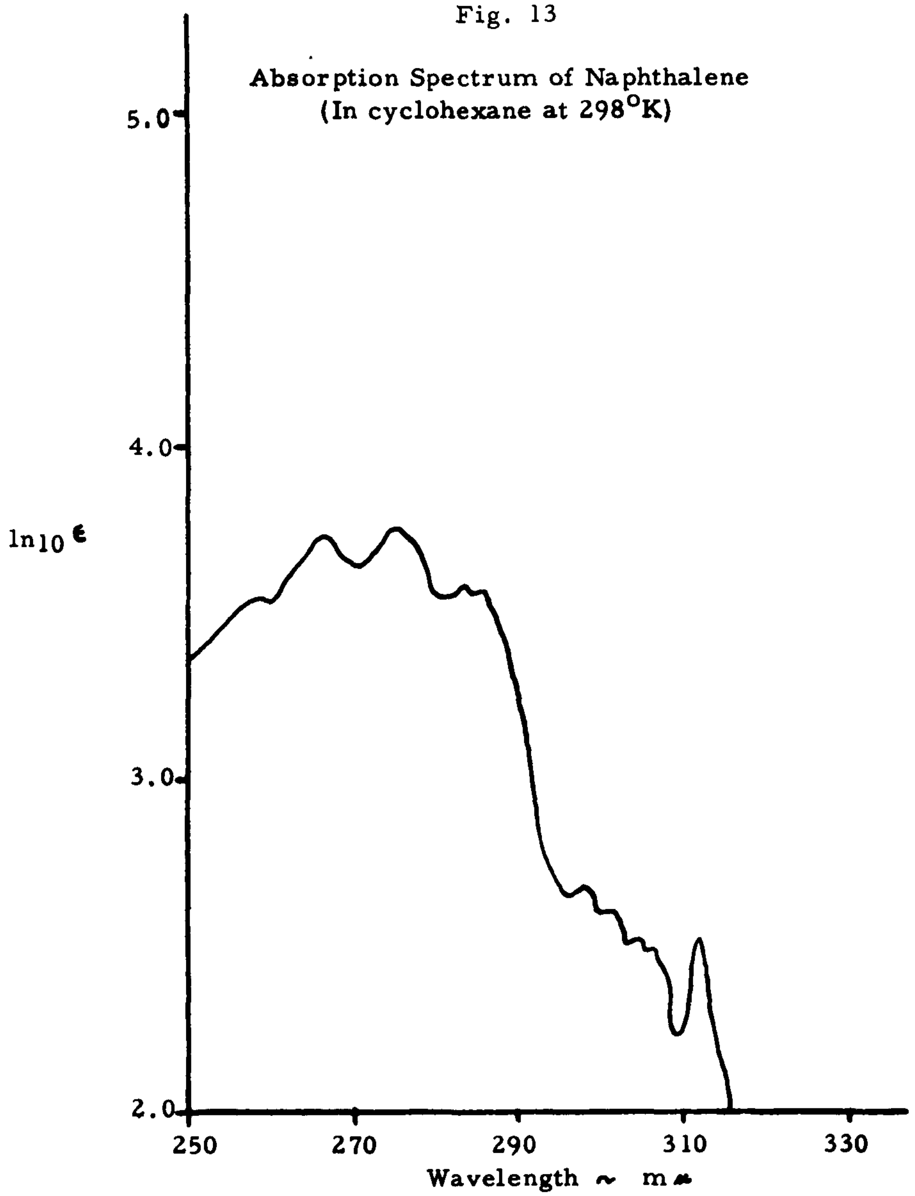
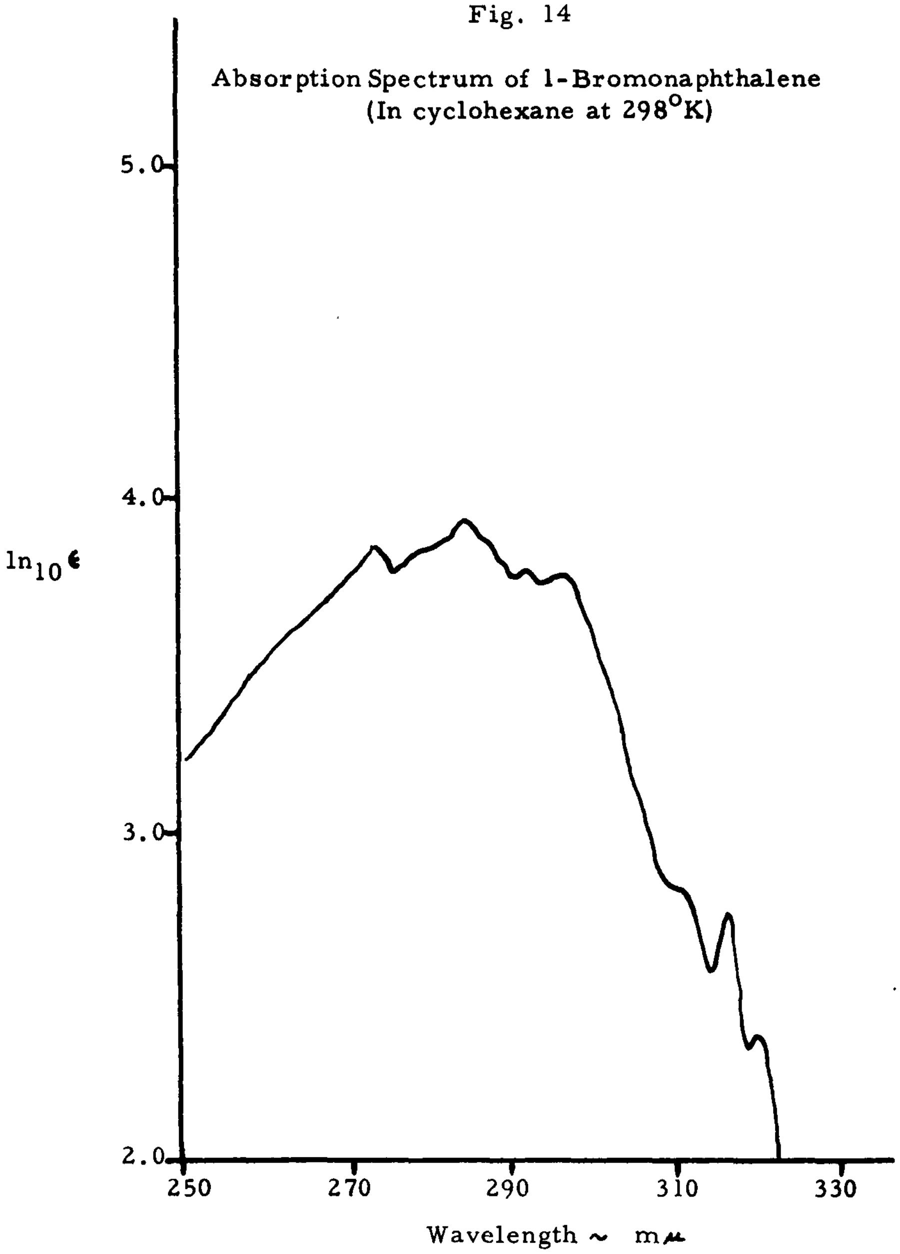


Fig. 13

Absorption Spectrum of Naphthalene
(In cyclohexane at 298°K)

Fig. 14

Absorption Spectrum of 1-Bromonaphthalene
(In cyclohexane at 298°K)



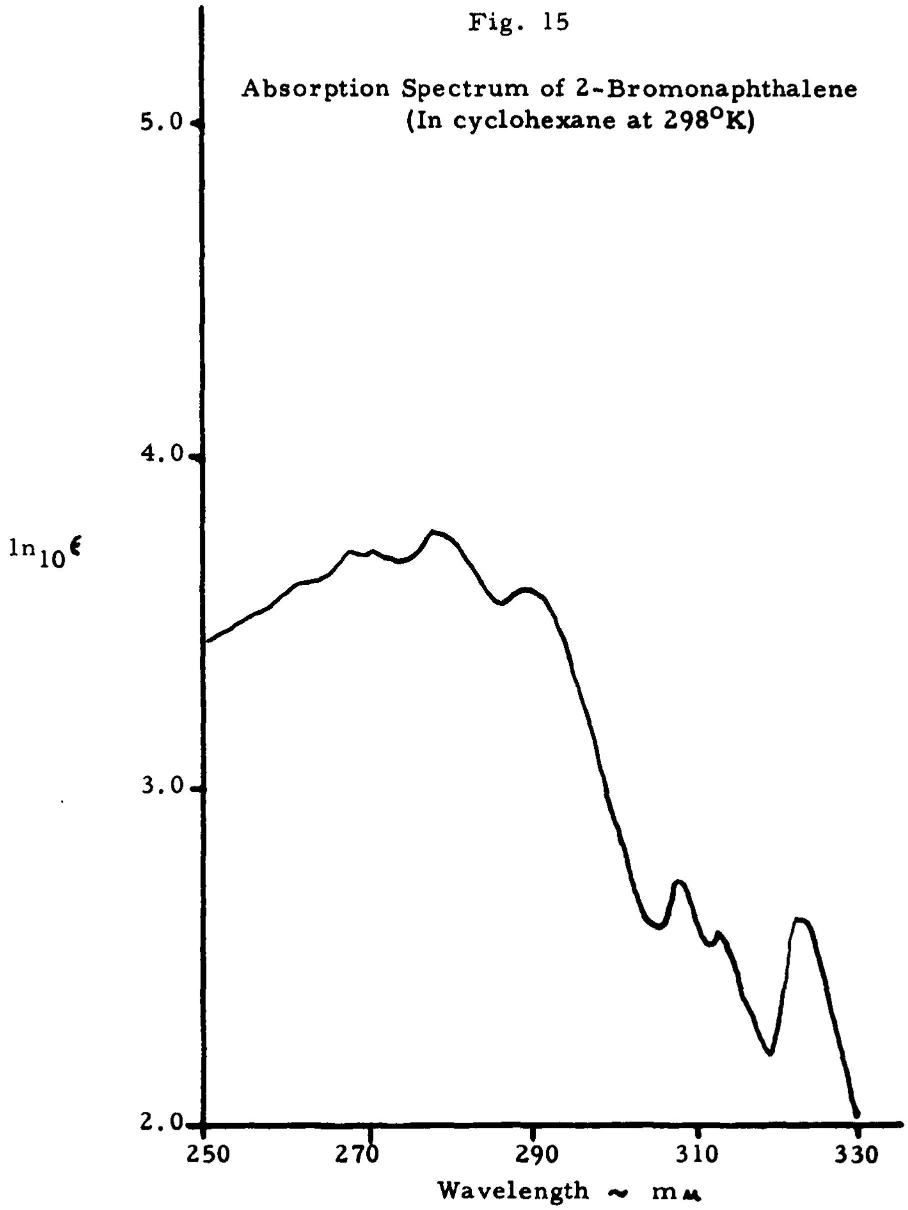


Fig. 15

Absorption Spectrum of 2-Bromonaphthalene
(In cyclohexane at 298°K)

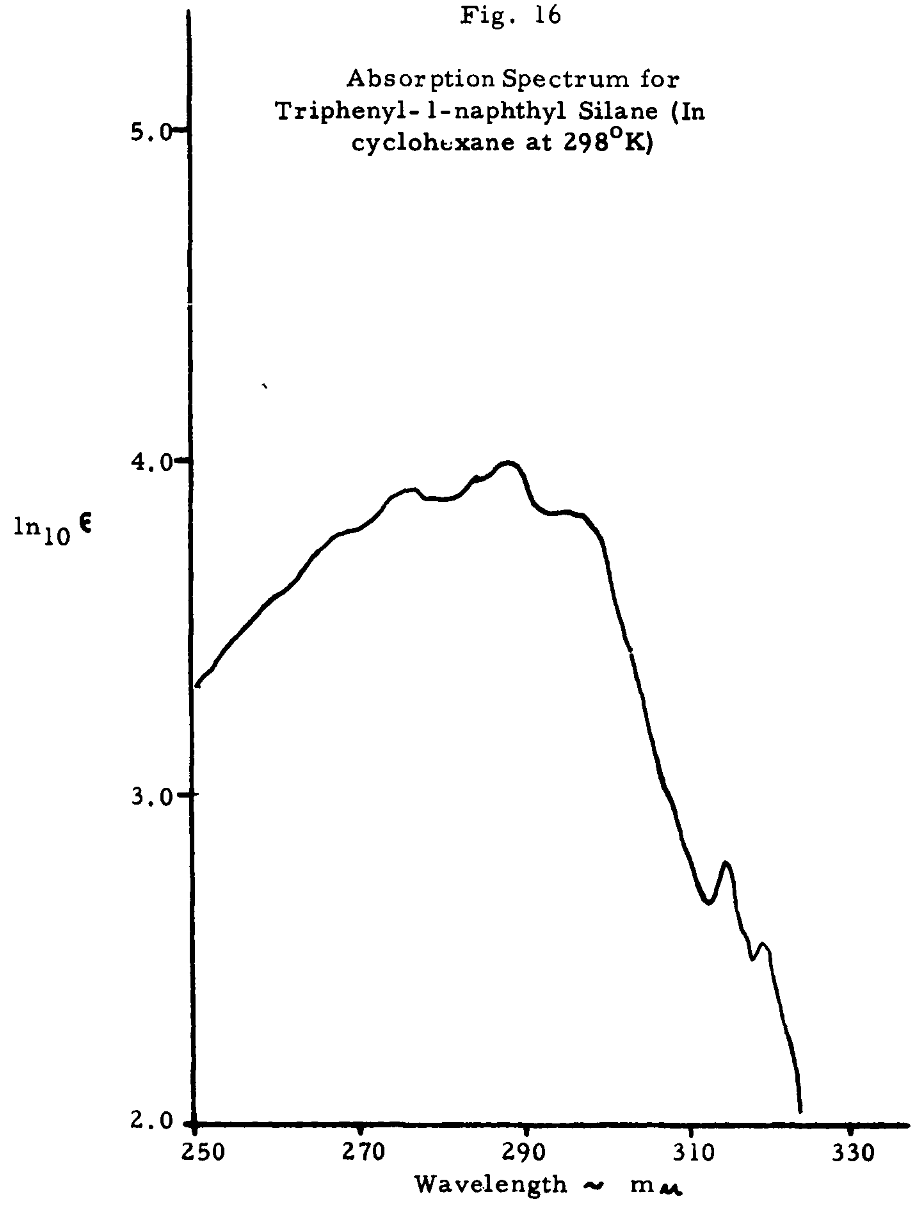


Fig. 16

Absorption Spectrum for Triphenyl-1-naphthyl Silane (In cyclohexane at 298°K)

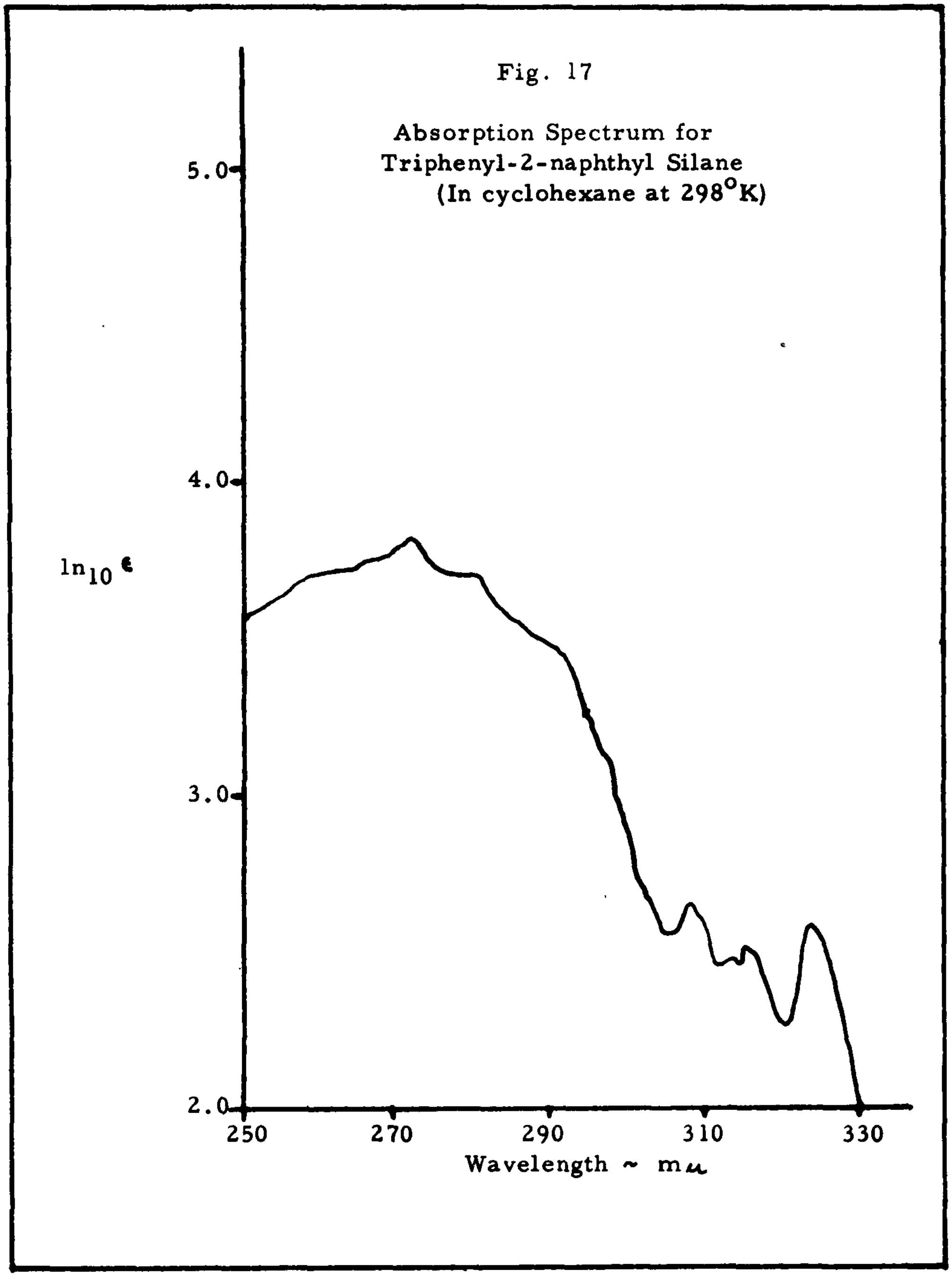


Fig. 17

Absorption Spectrum for Triphenyl-2-naphthyl Silane (In cyclohexane at 298°K)

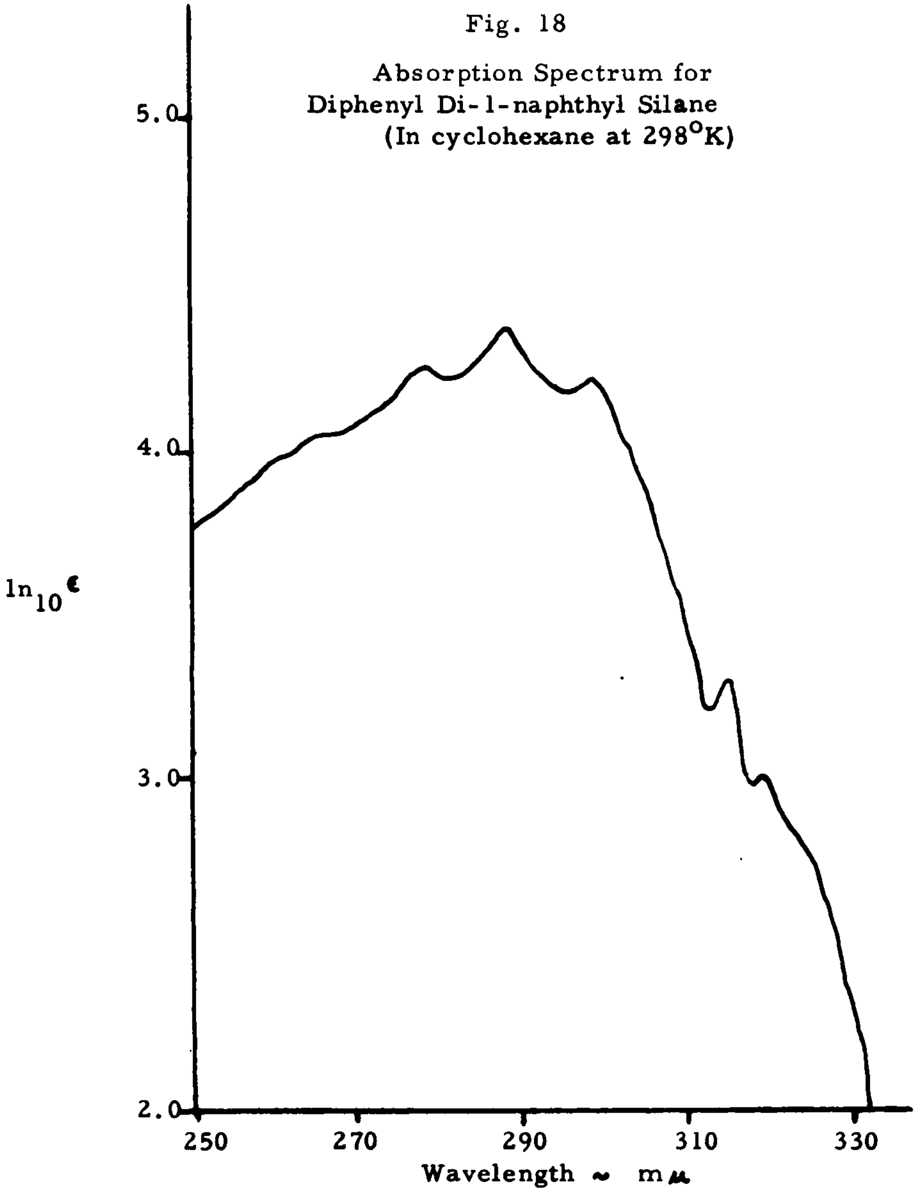


Fig. 18

Absorption Spectrum for Diphenyl Di-1-naphthyl Silane (In cyclohexane at 298°K)

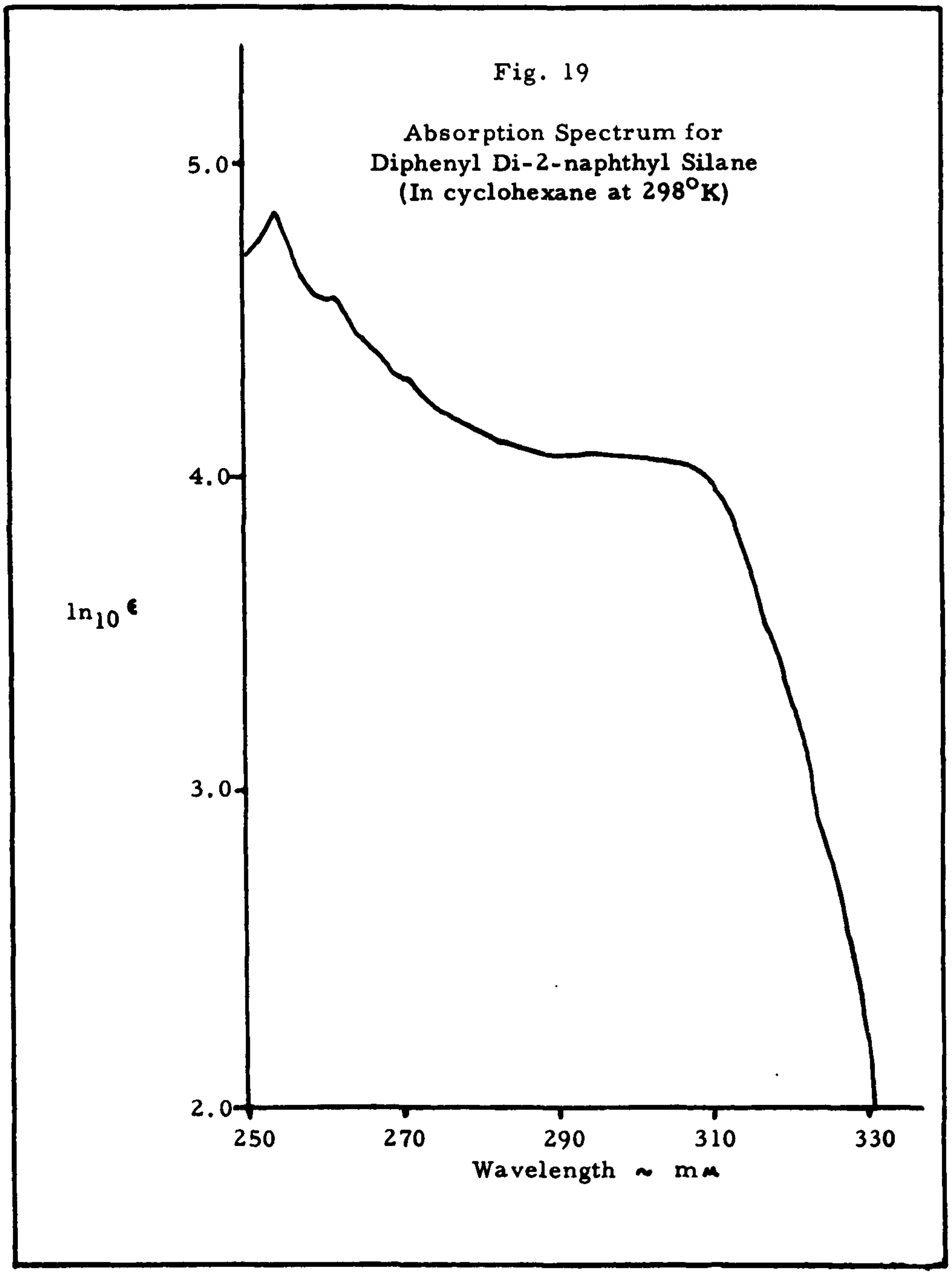


Fig. 19

Absorption Spectrum for
Diphenyl Di-2-naphthyl Silane
(In cyclohexane at 298°K)

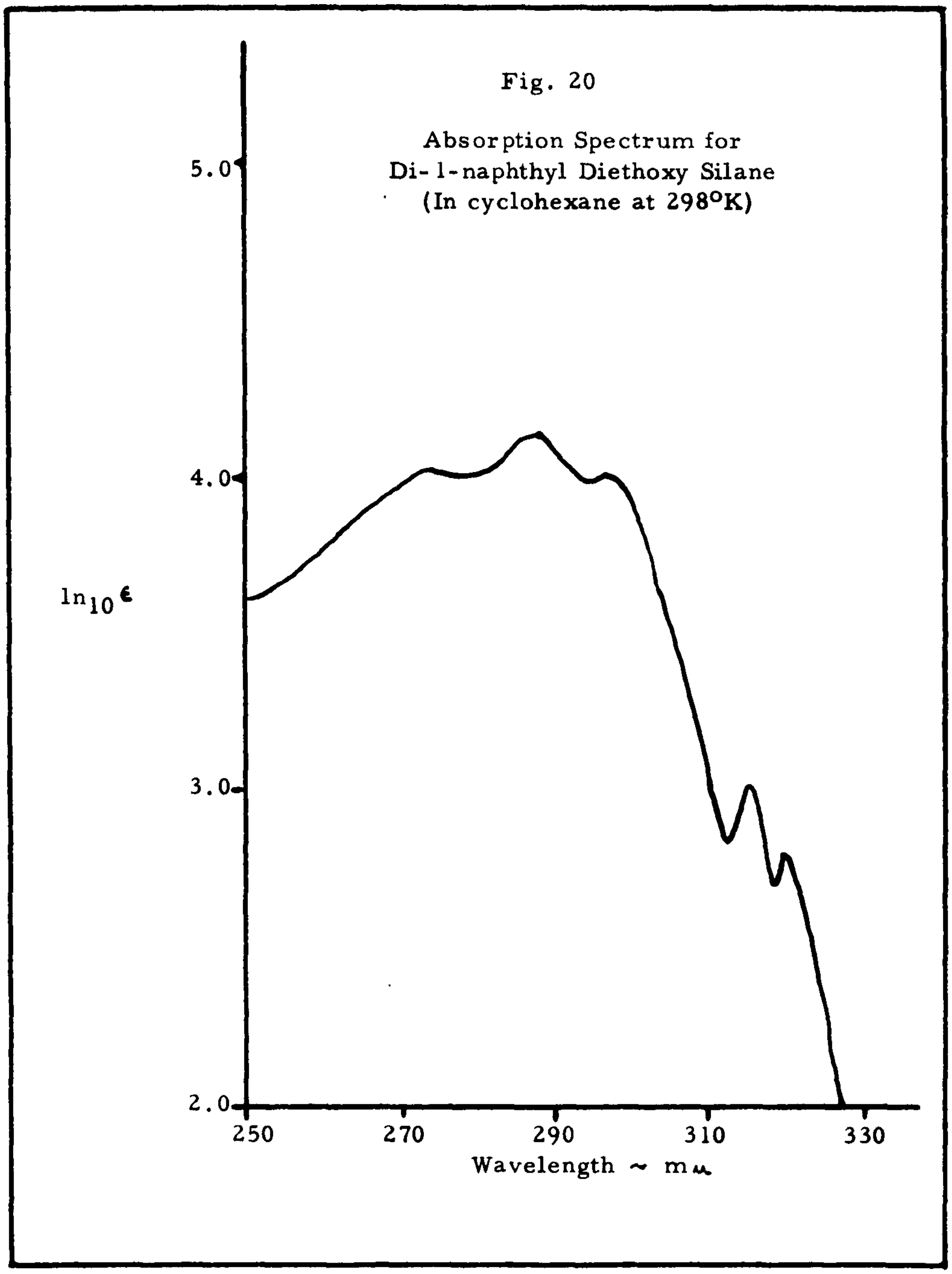


Fig. 20

Absorption Spectrum for
Di-1-naphthyl Diethoxy Silane
(In cyclohexane at 298°K)

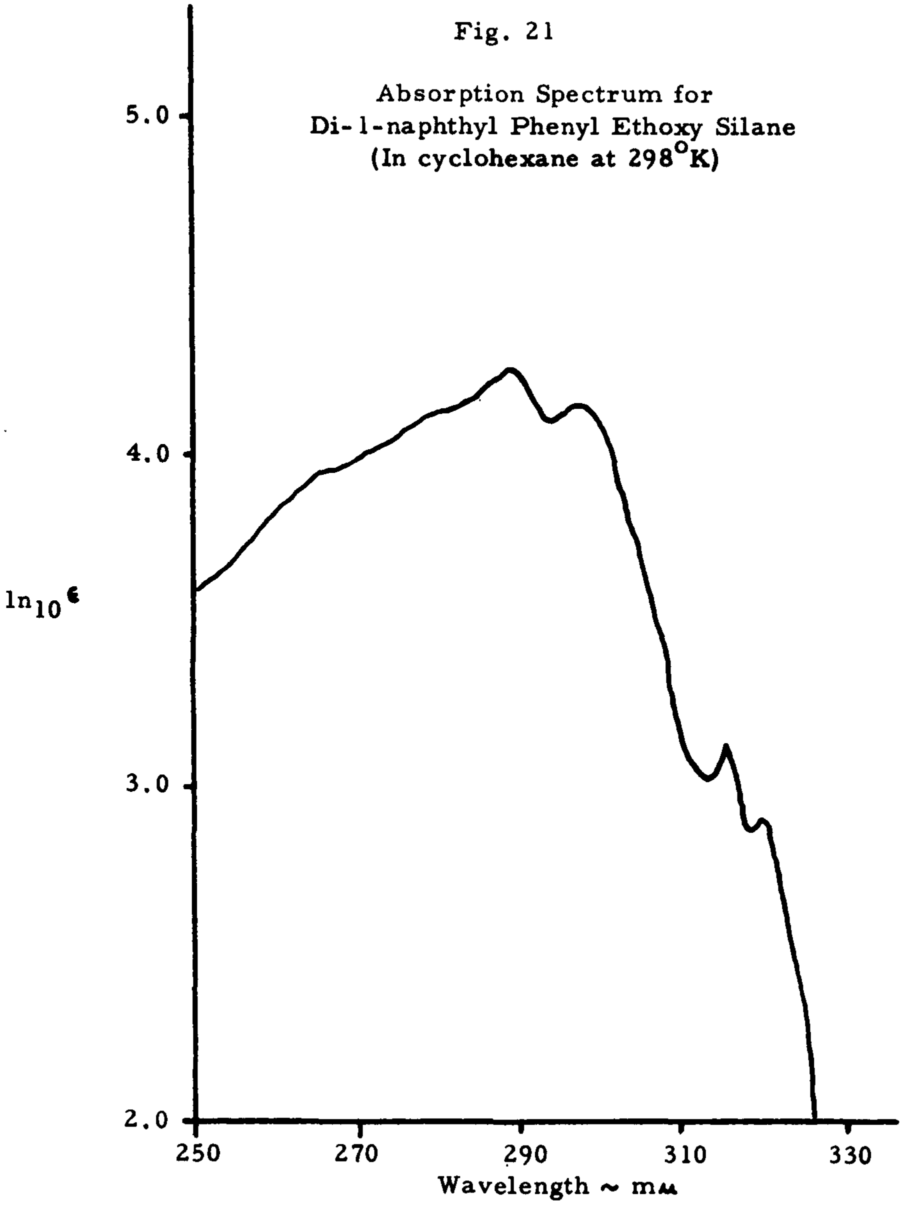


Fig. 21

Absorption Spectrum for
Di-1-naphthyl Phenyl Ethoxy Silane
(In cyclohexane at 298°K)

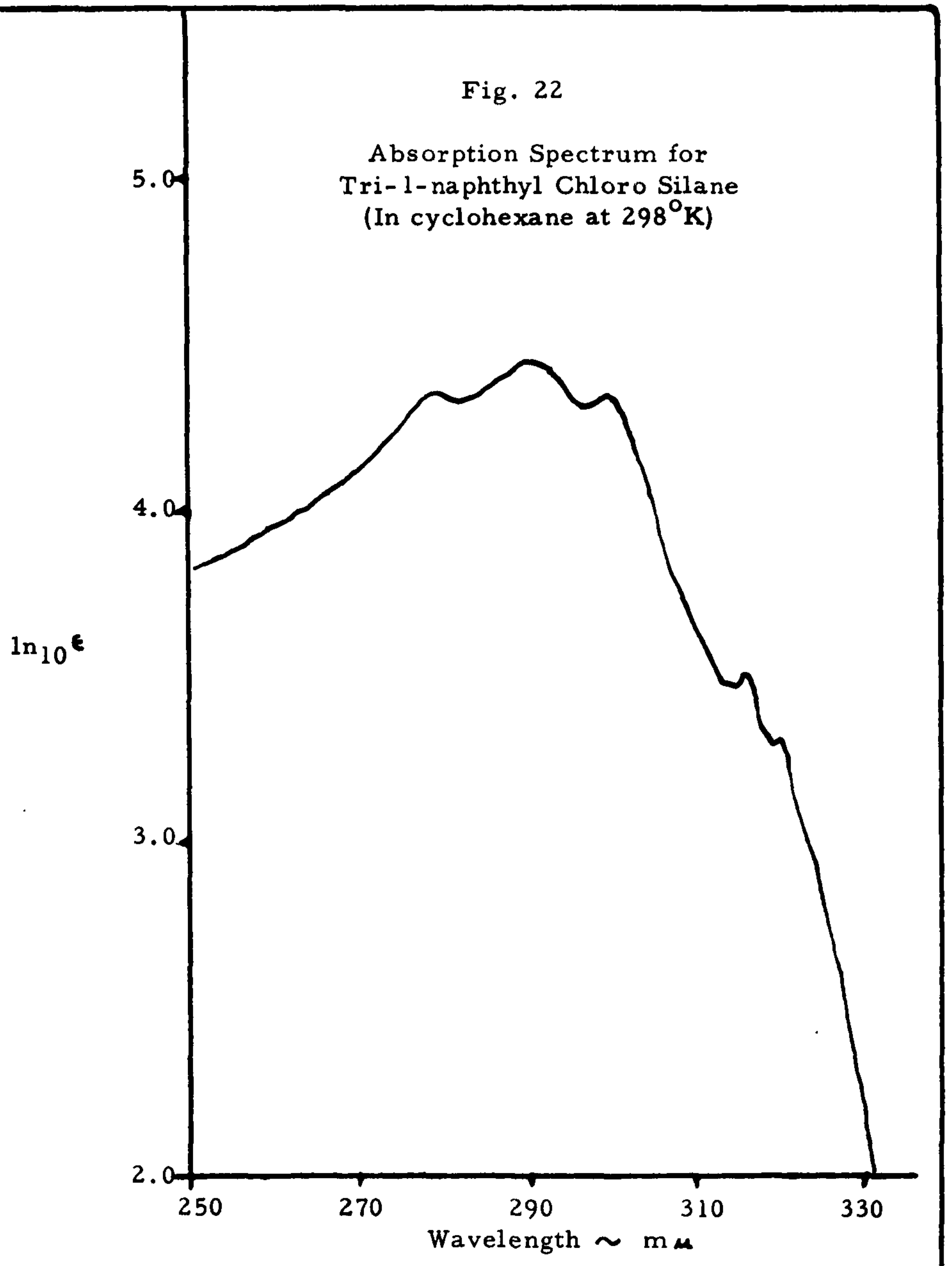


Fig. 22

Absorption Spectrum for
Tri-1-naphthyl Chloro Silane
(In cyclohexane at 298°K)

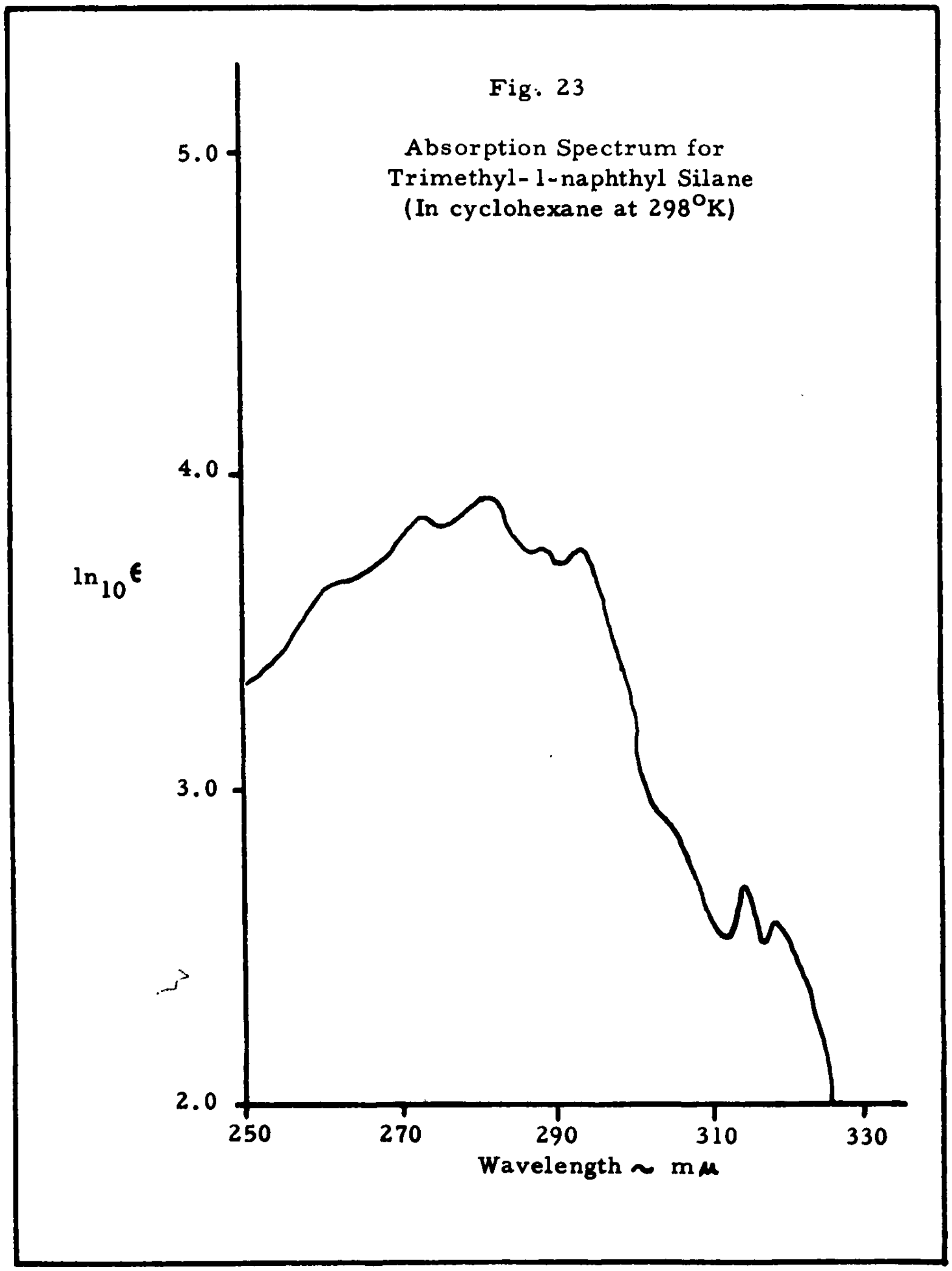


Fig. 23

Absorption Spectrum for Trimethyl-1-naphthyl Silane (In cyclohexane at 298°K)

# Appendix B

## Fluorescent Emission Spectra of Naphthyl Silanes

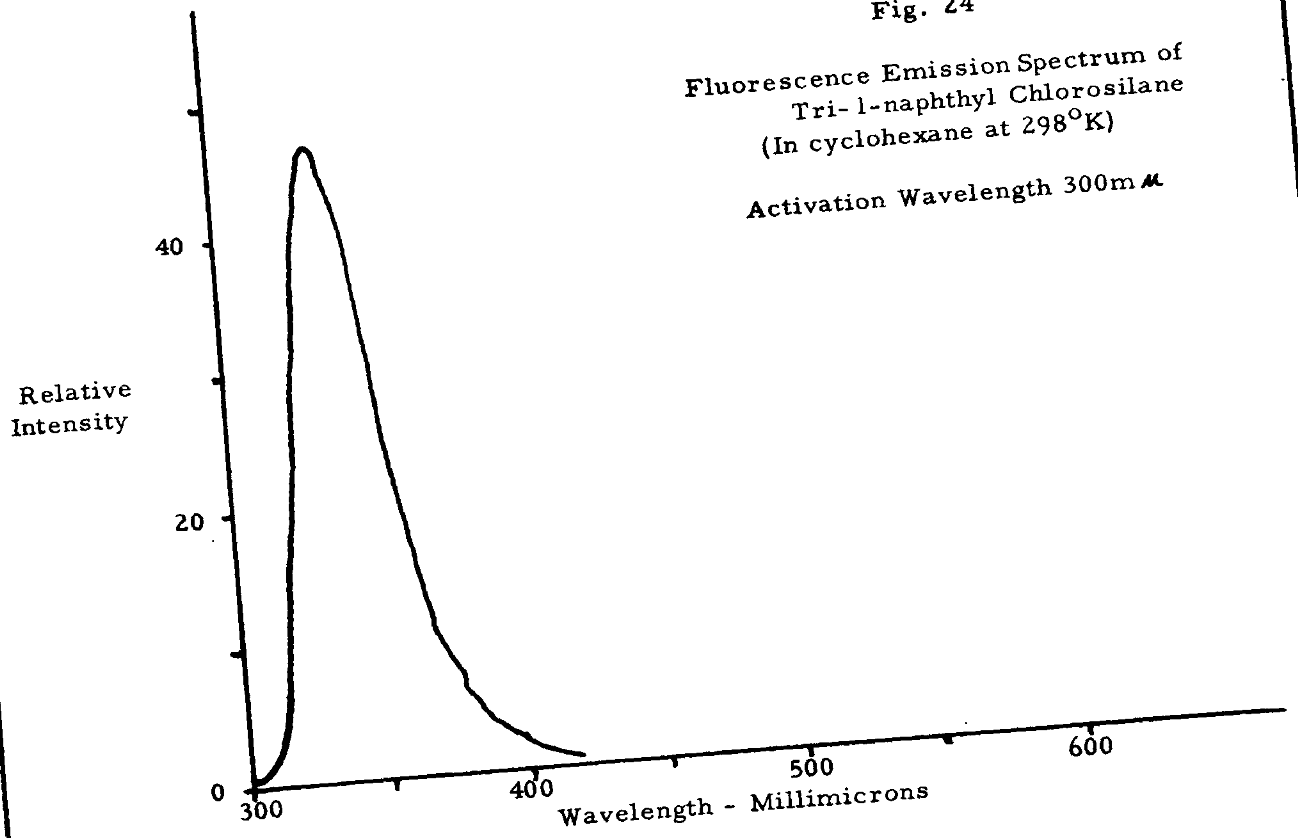


Fig. 24

Fluorescence Emission Spectrum of
Tri-1-naphthyl Chlorosilane
(In cyclohexane at 298°K)

Activation Wavelength 300m$\mu$

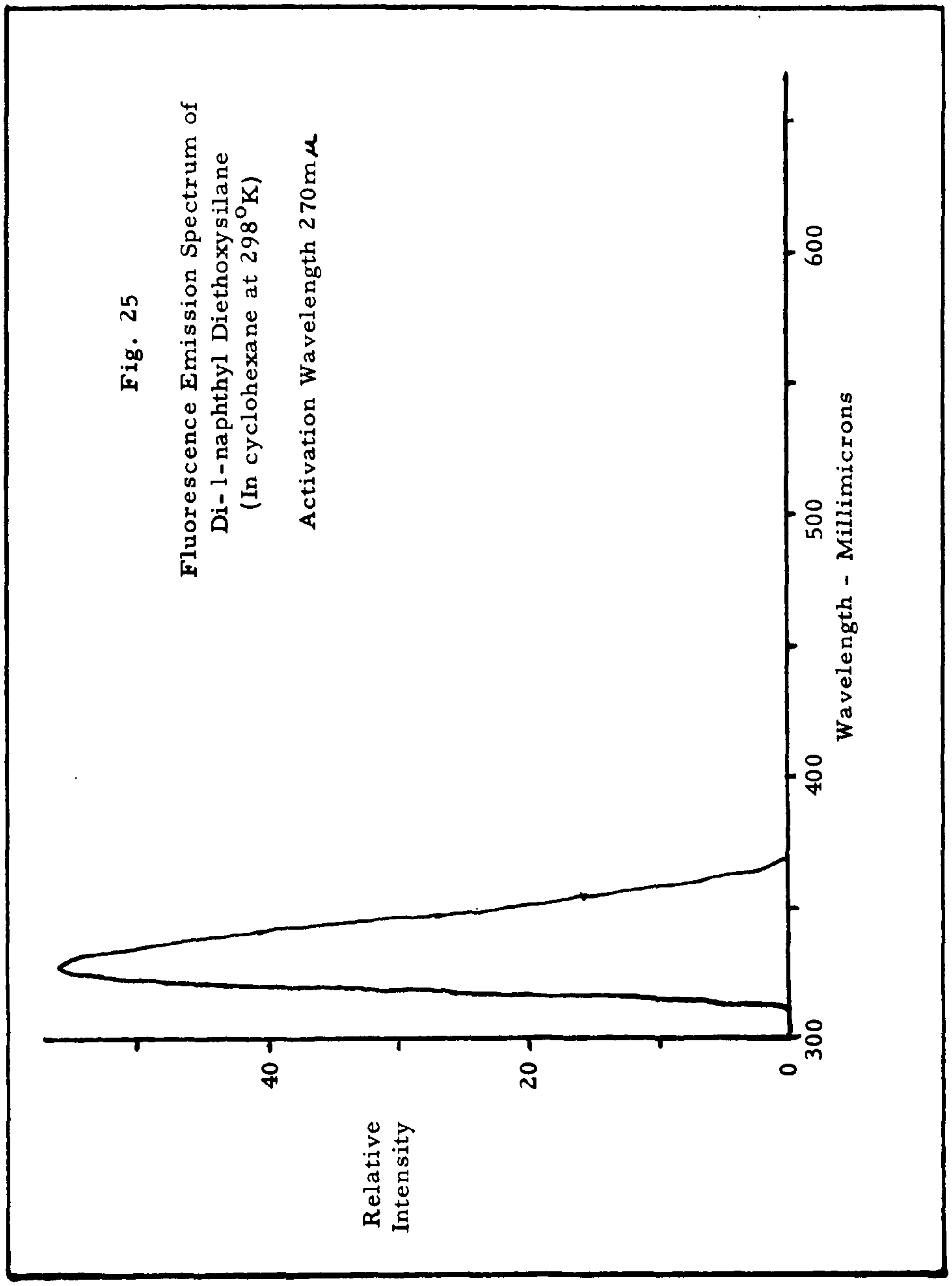


Fig. 25

Fluorescence Emission Spectrum of
Di-1-naphthyl Diethoxysilane
(In cyclohexane at 298°K)

Activation Wavelength 270mμ

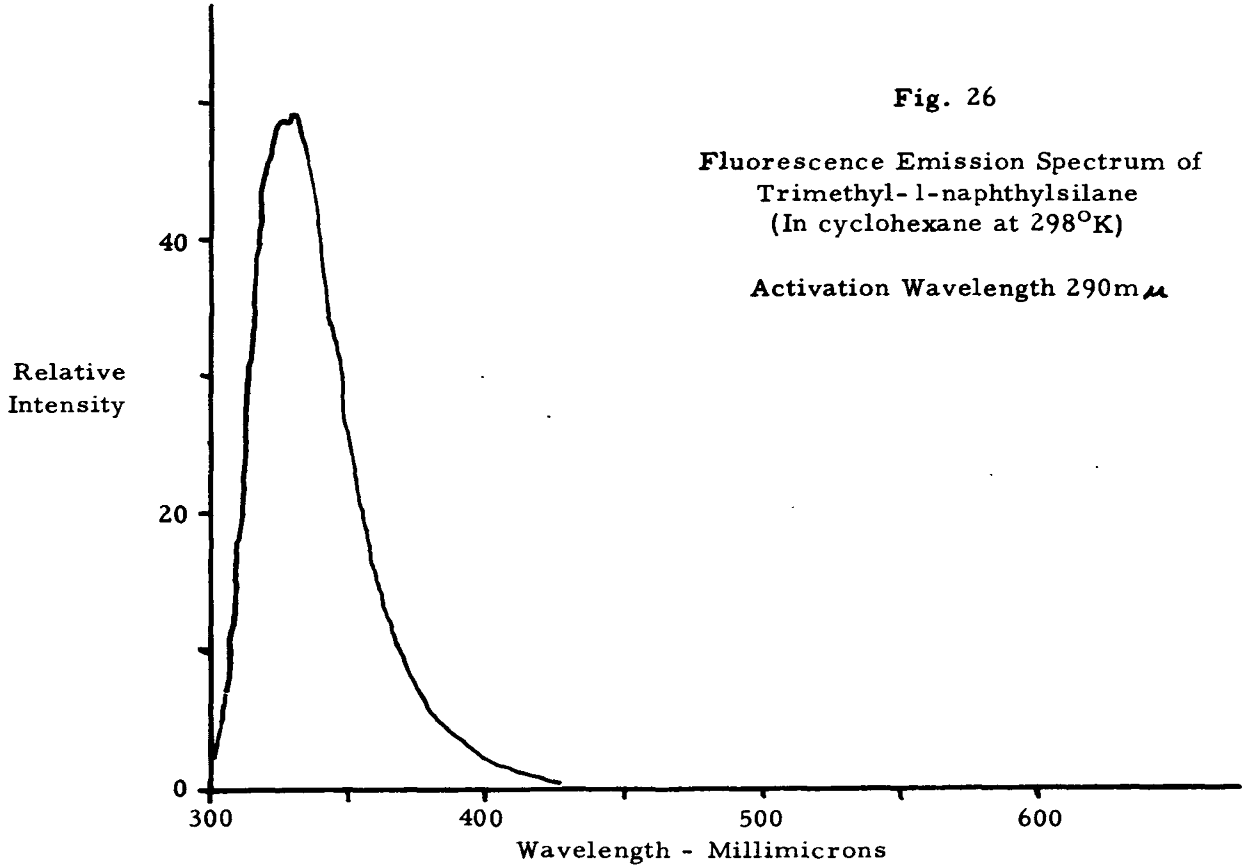


**Fig. 26**

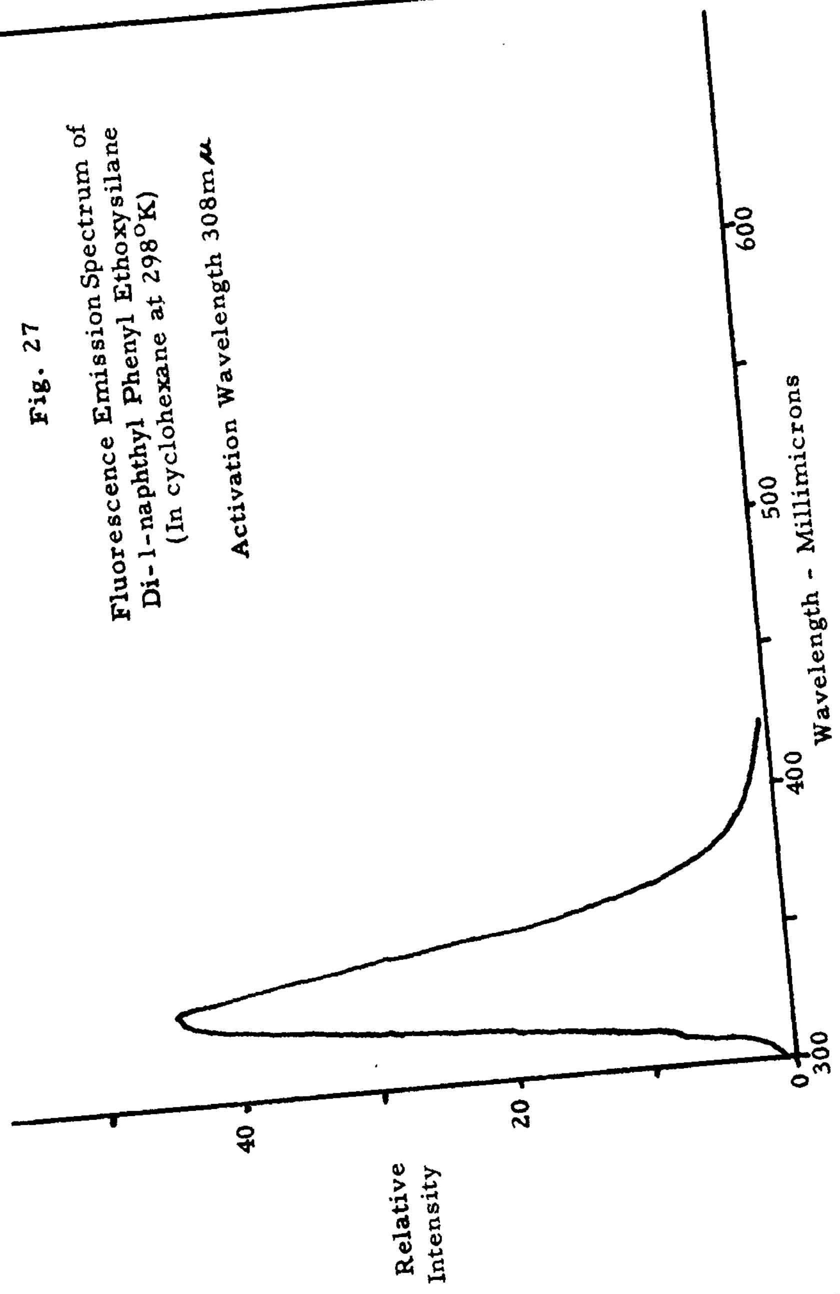
Fluorescence Emission Spectrum of Trimethyl-1-naphthylsilane (In cyclohexane at 298°K)

Activation Wavelength 290mμ

Fig. 27

Fluorescence Emission Spectrum of Di-1-naphthyl Phenyl Ethoxysilane (In cyclohexane at 298°K)

Activation Wavelength 308mμ



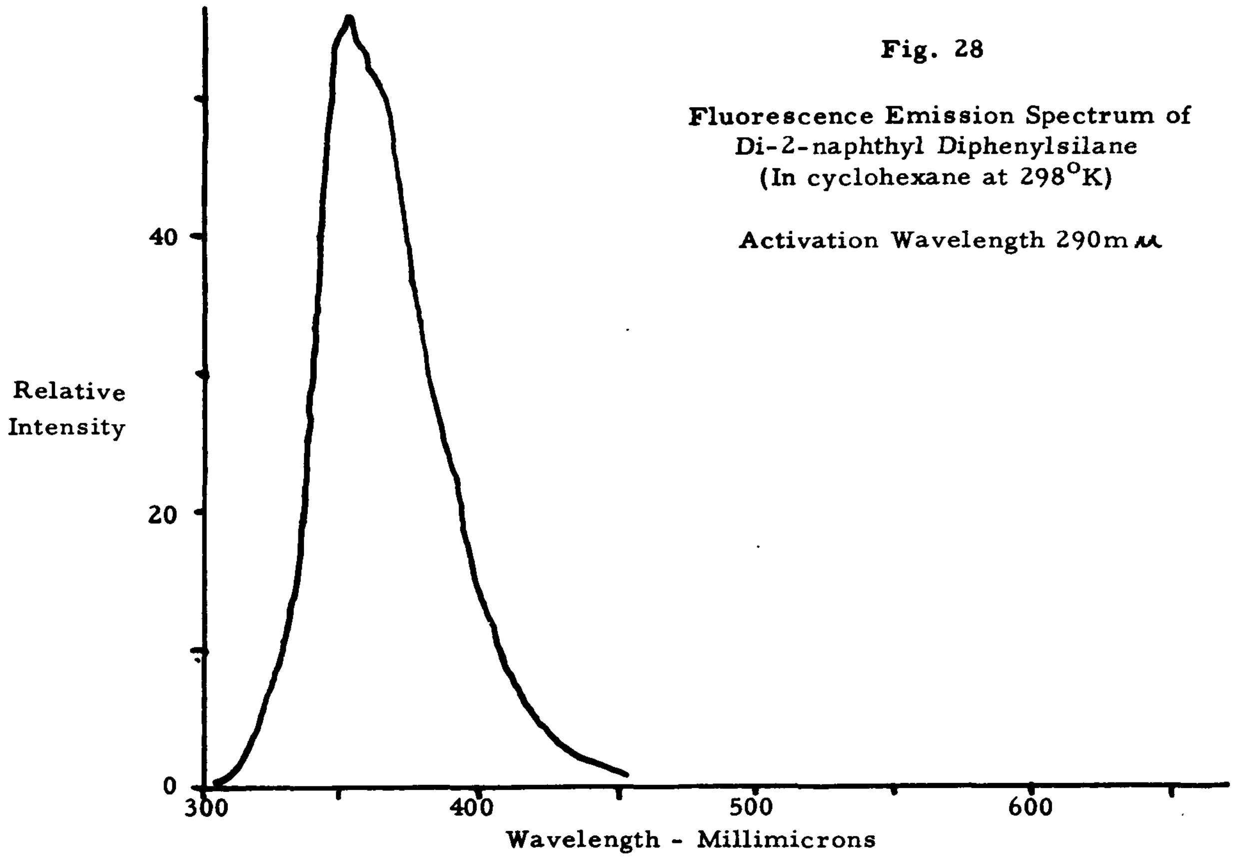


Fig. 28

Fluorescence Emission Spectrum of
Di-2-naphthyl Diphenylsilane
(In cyclohexane at 298°K)

Activation Wavelength 290m$\mu$

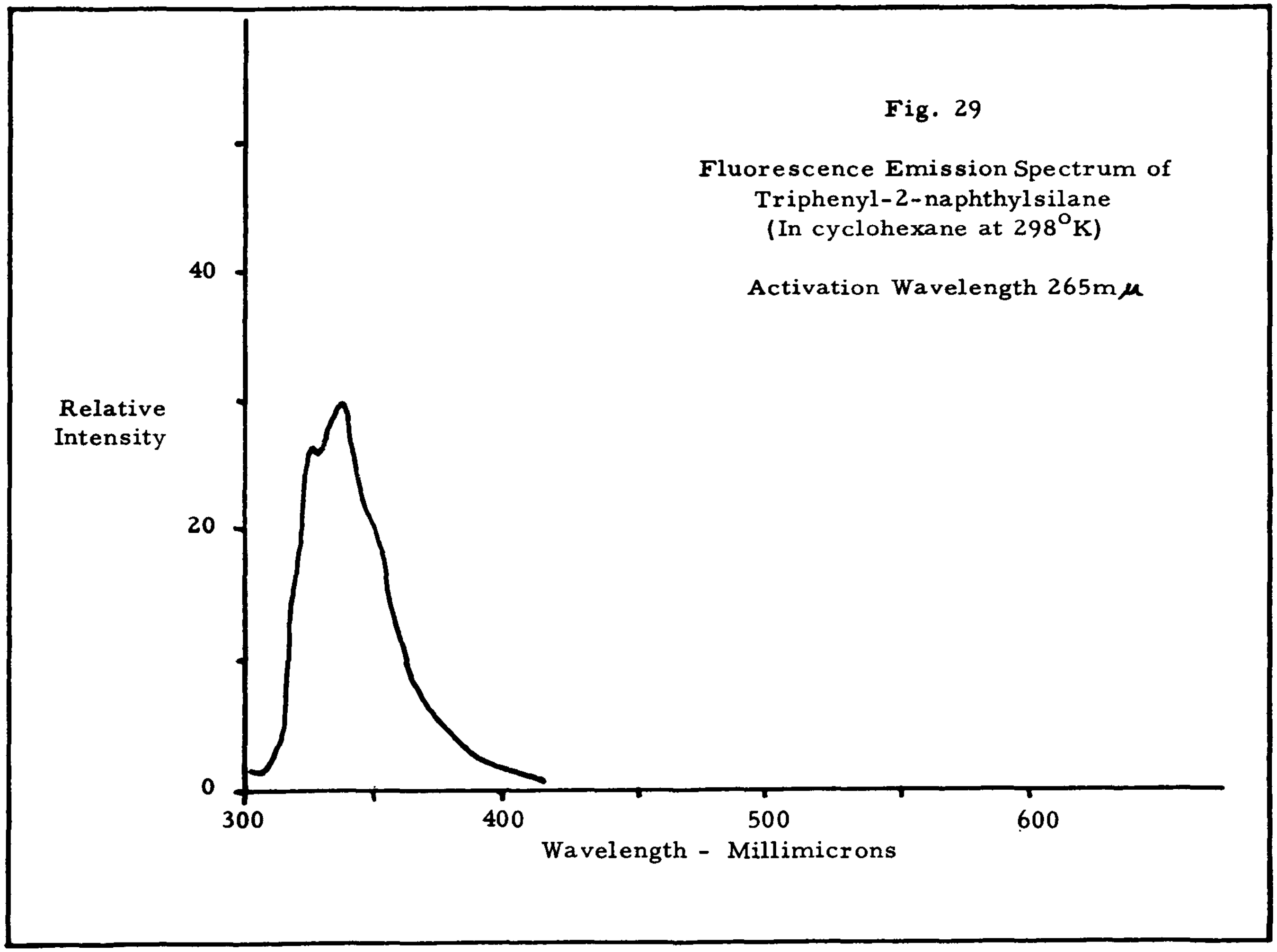


Fig. 29

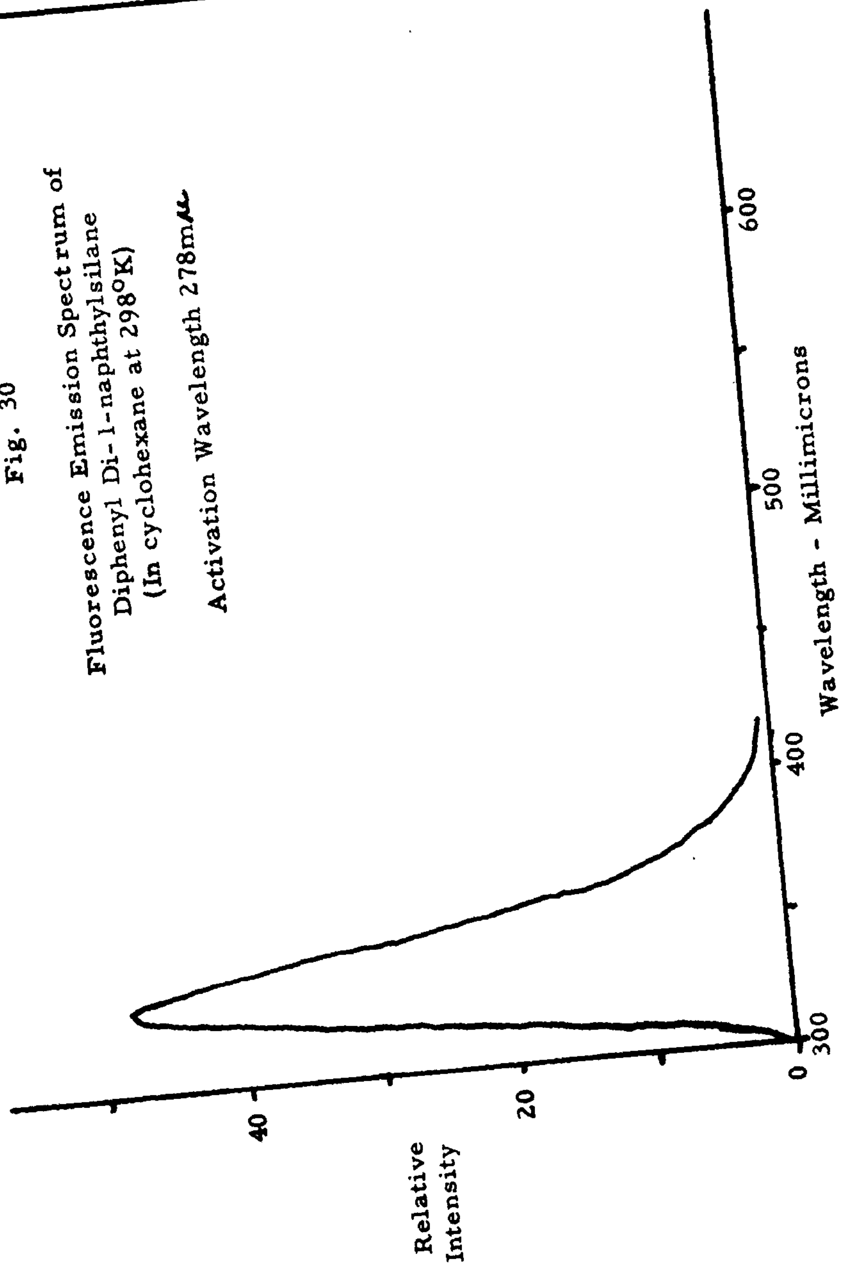
Fluorescence Emission Spectrum of
Triphenyl-2-naphthylsilane
(In cyclohexane at 298°K)

Activation Wavelength 265mμ

Fig. 30

Fluorescence Emission Spectrum of Diphenyl Di-1-naphthylsilane (In cyclohexane at 298°K)

Activation Wavelength 278mμ



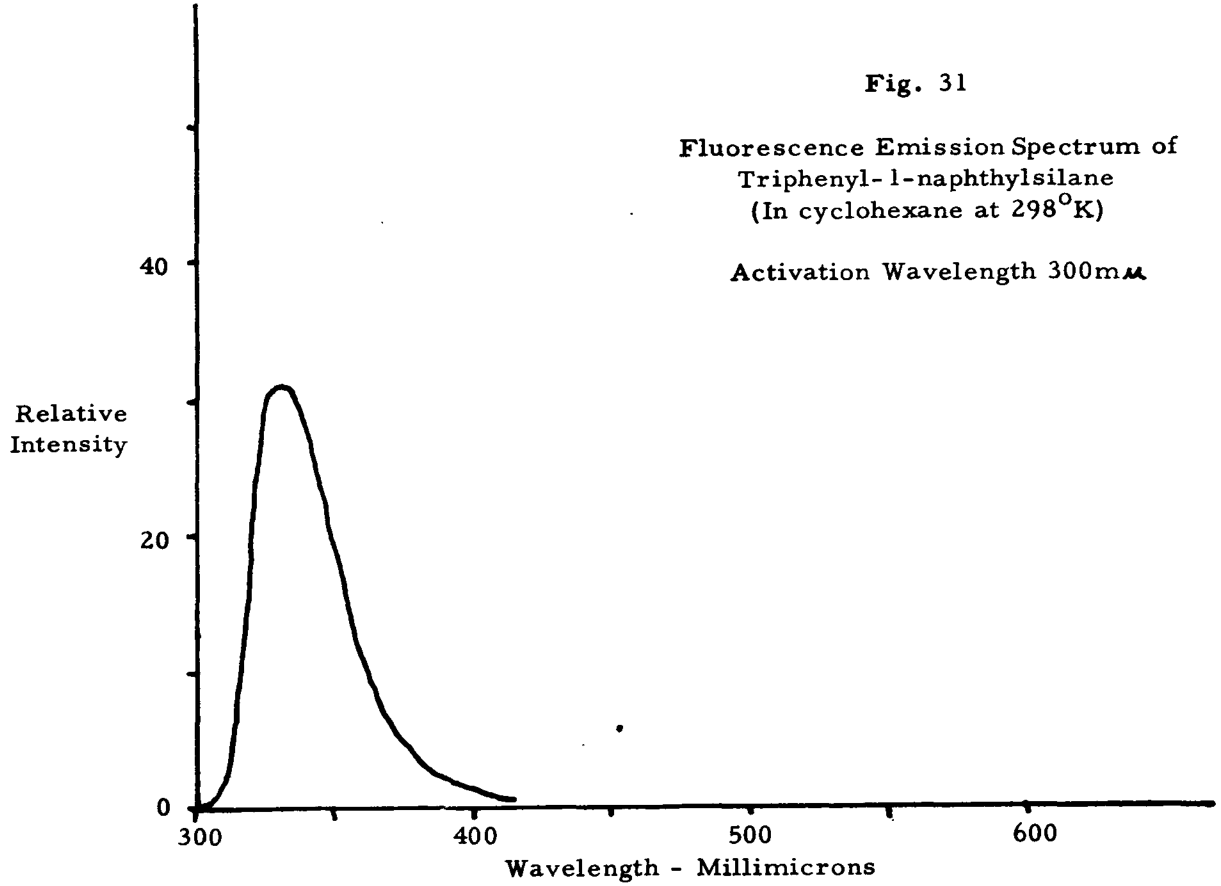


**Fig. 31**

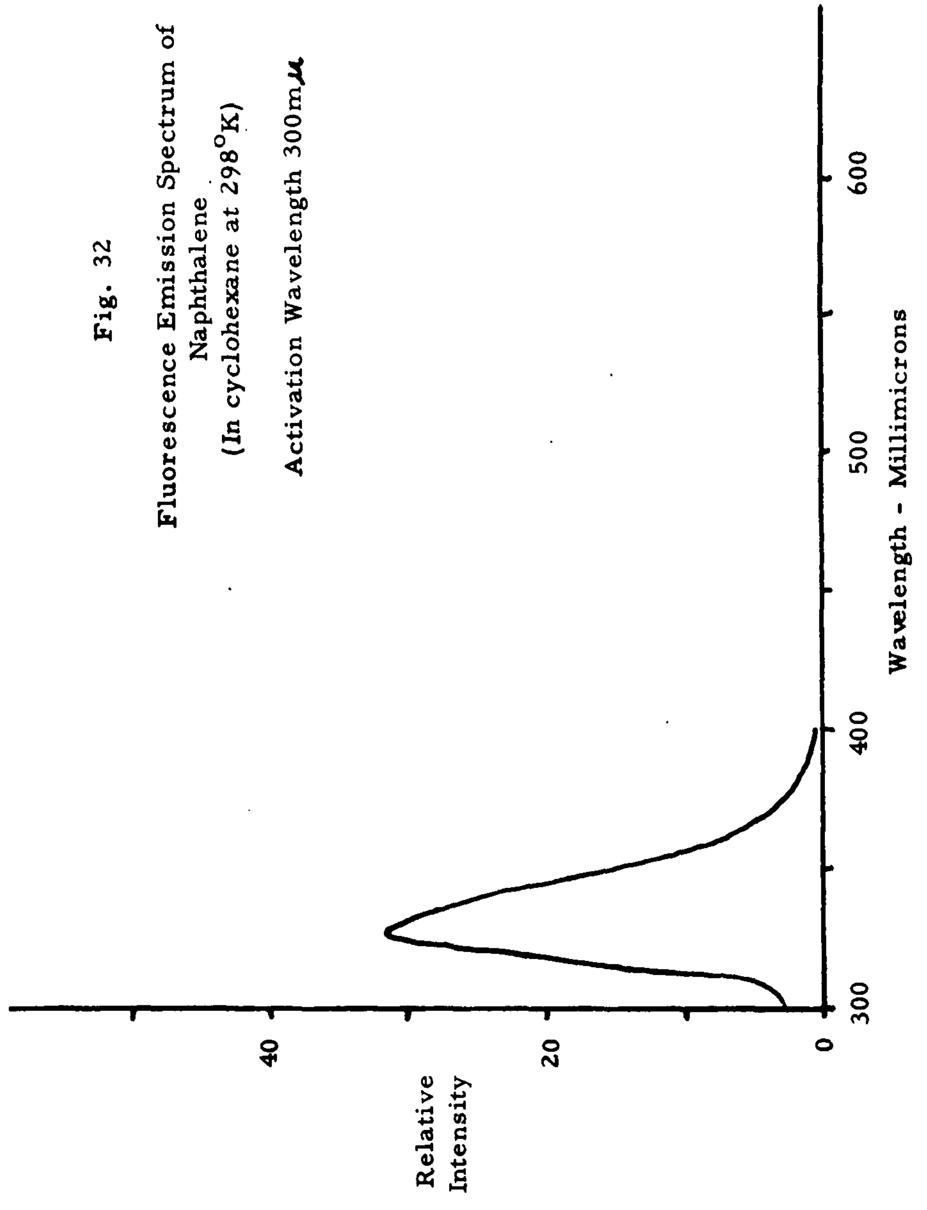
Fluorescence Emission Spectrum of
Triphenyl-1-naphthylsilane
(In cyclohexane at 298°K)

Activation Wavelength 300mμ

Fig. 32

Fluorescence Emission Spectrum of Naphthalene
(In cyclohexane at 298°K)

Activation Wavelength 300mμ



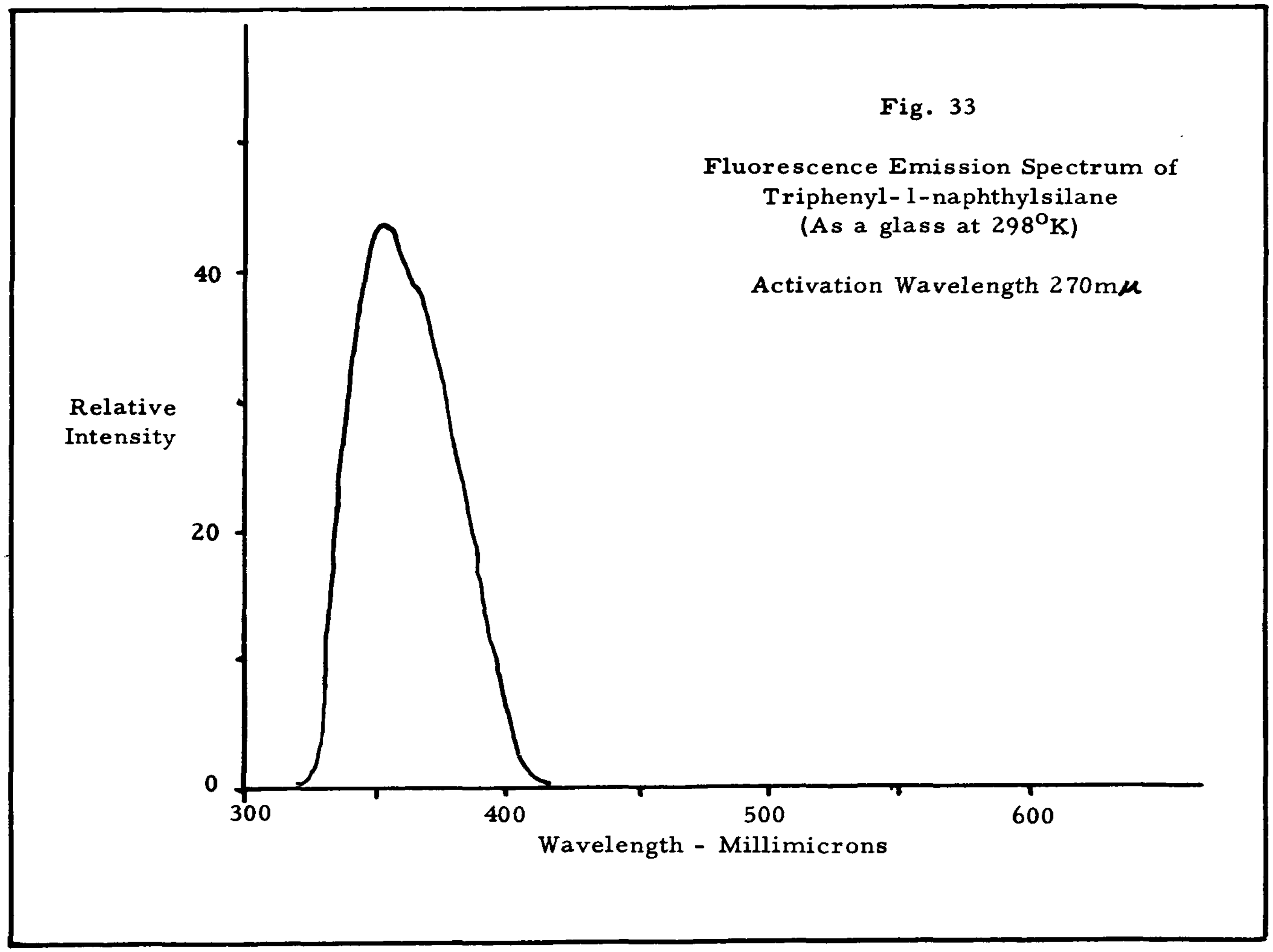


Fig. 33

Fluorescence Emission Spectrum of
Triphenyl-1-naphthylsilane
(As a glass at 298$^{o}$K)

Activation Wavelength 270m$\mu$

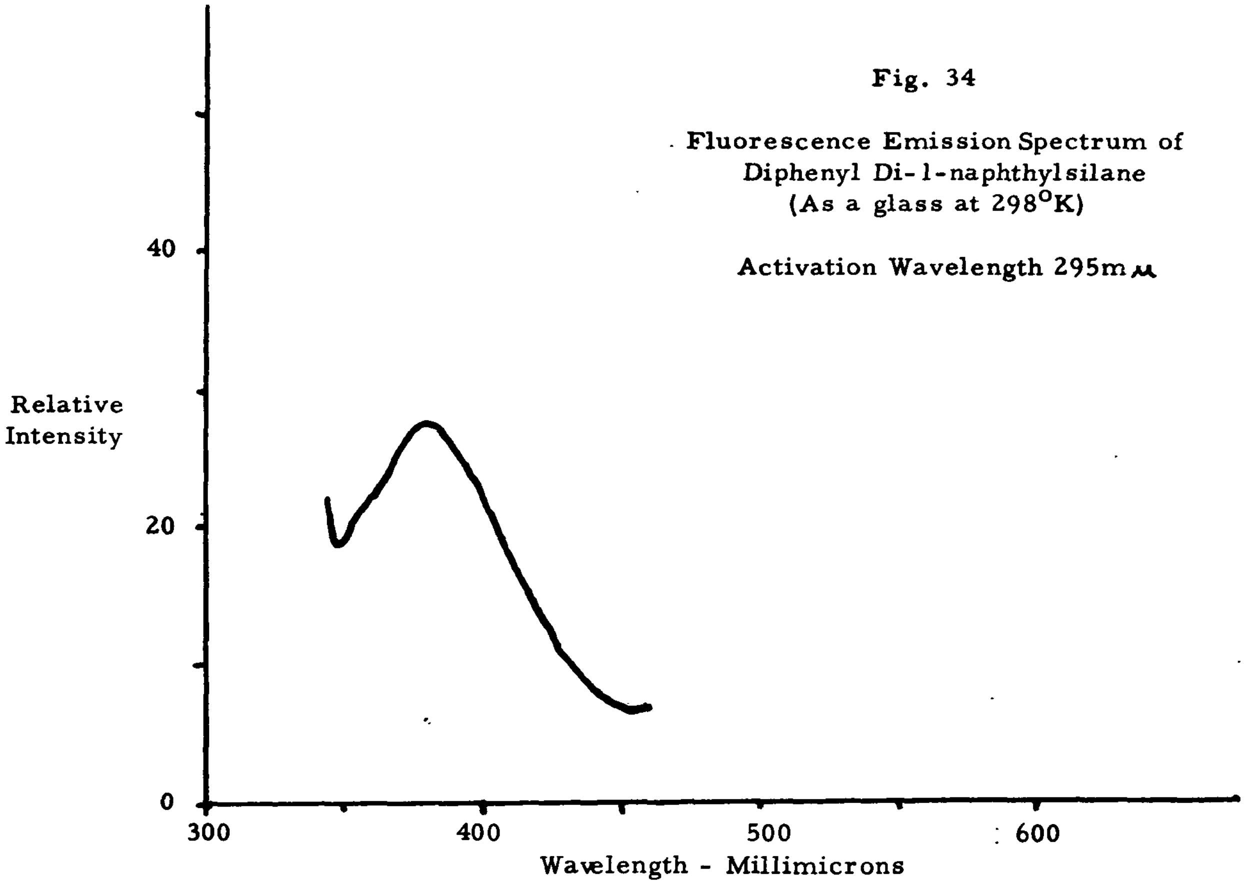


Fig. 34

Fluorescence Emission Spectrum of Diphenyl Di-1-naphthylsilane (As a glass at 298°K)

Activation Wavelength 295mμ

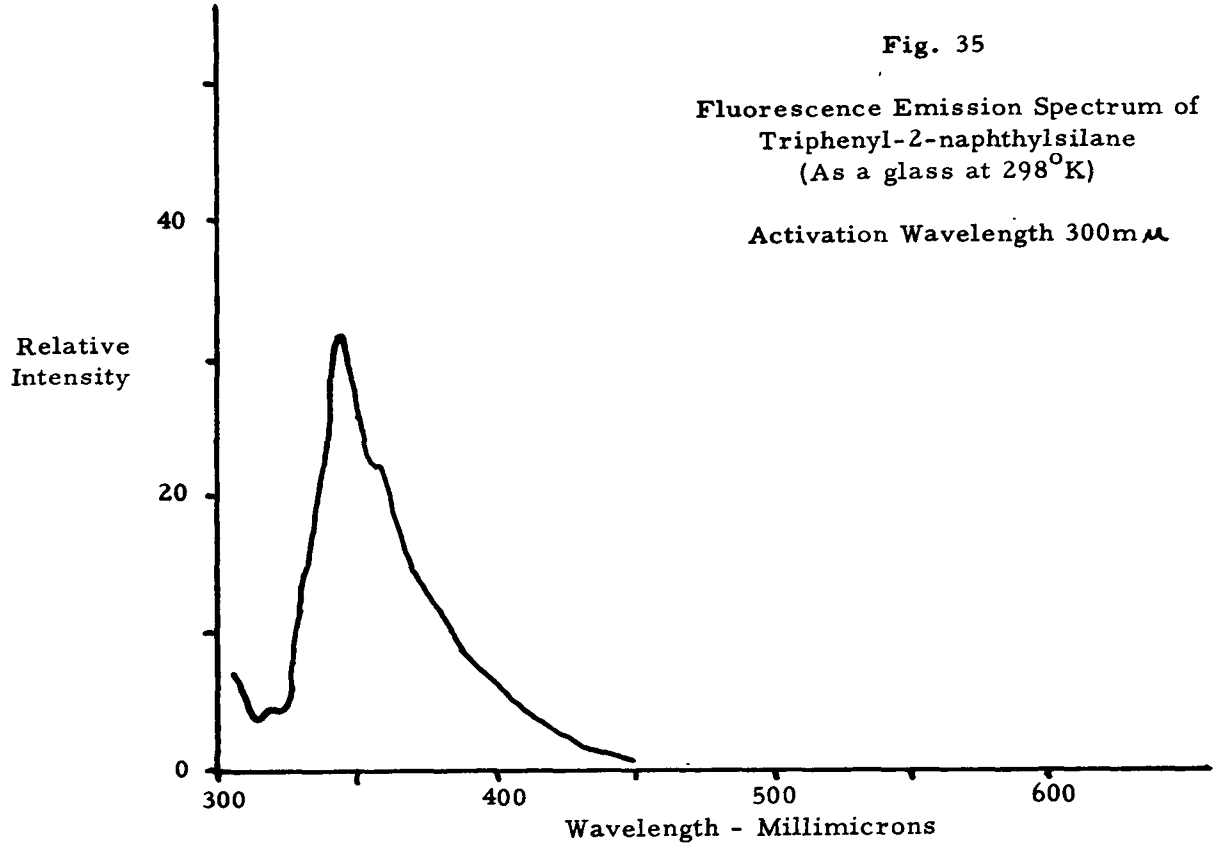


Fig. 35

Fluorescence Emission Spectrum of
Triphenyl-2-naphthylsilane
(As a glass at 298°K)

Activation Wavelength 300mμ

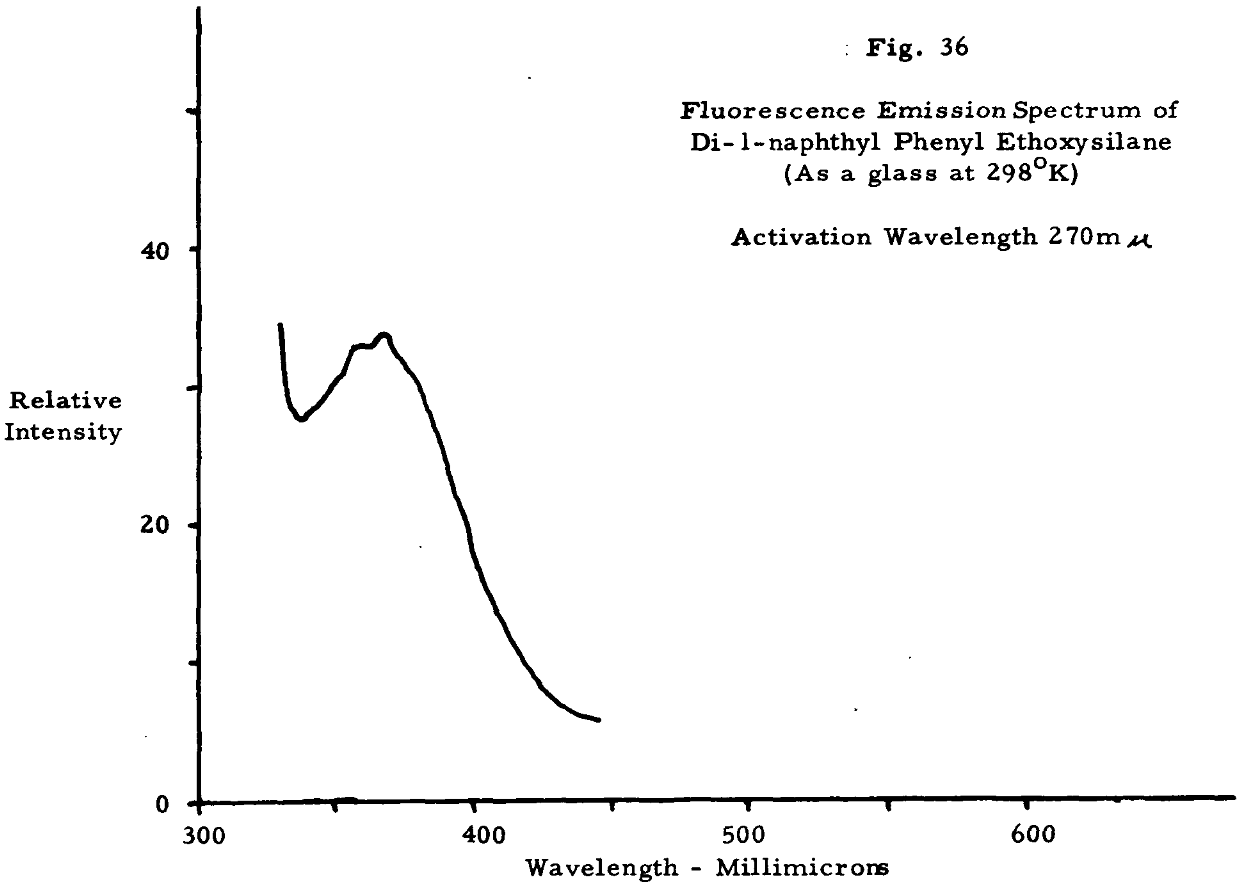


**Fig. 36**

Fluorescence Emission Spectrum of
Di-1-naphthyl Phenyl Ethoxysilane
(As a glass at 298°K)

Activation Wavelength 270m$\mu$

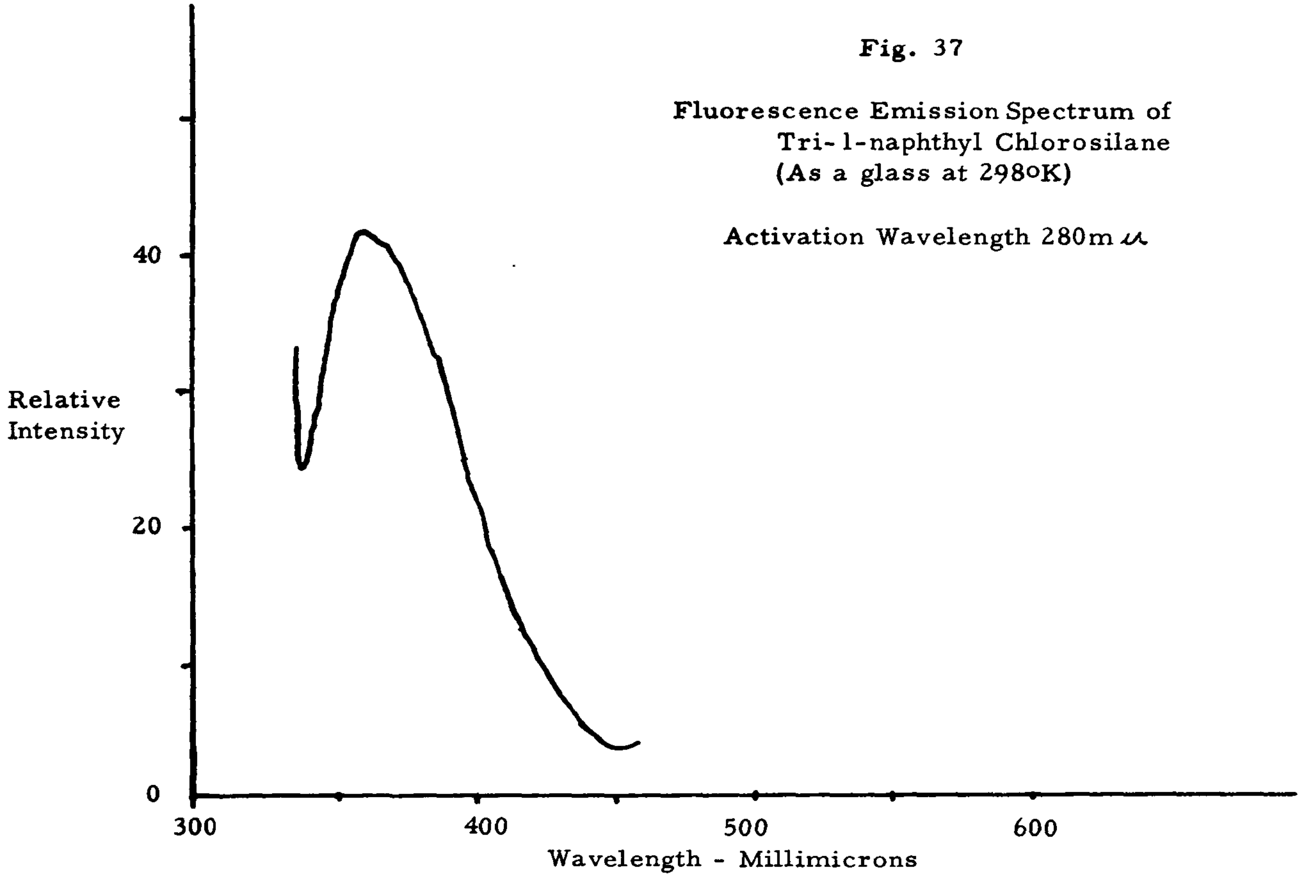


**Fig. 37**

Fluorescence Emission Spectrum of
Tri-1-naphthyl Chlorosilane
(As a glass at 298°K)

Activation Wavelength 280mμ

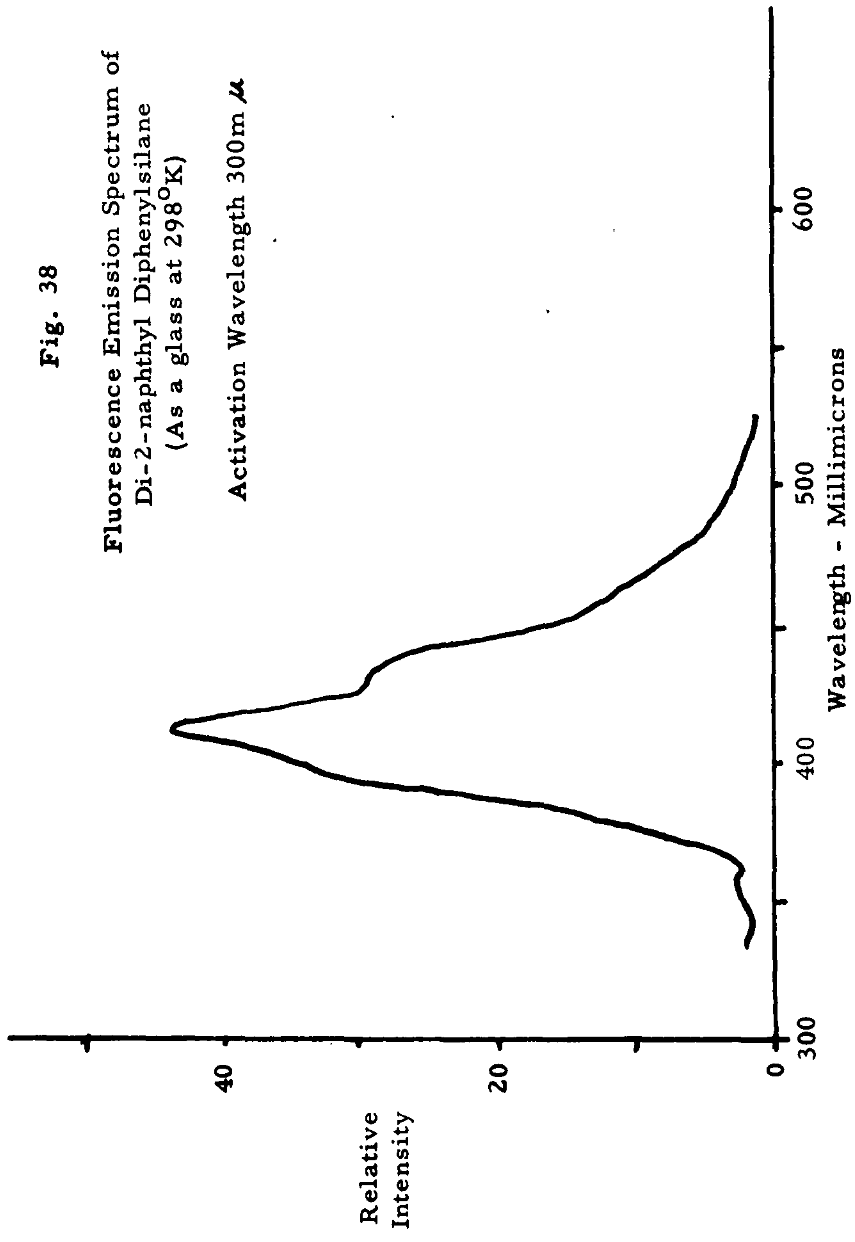


**Fig. 38**

Fluorescence Emission Spectrum of
Di-2-naphthyl Diphenylsilane
(As a glass at 298°K)

Activation Wavelength 300m μ

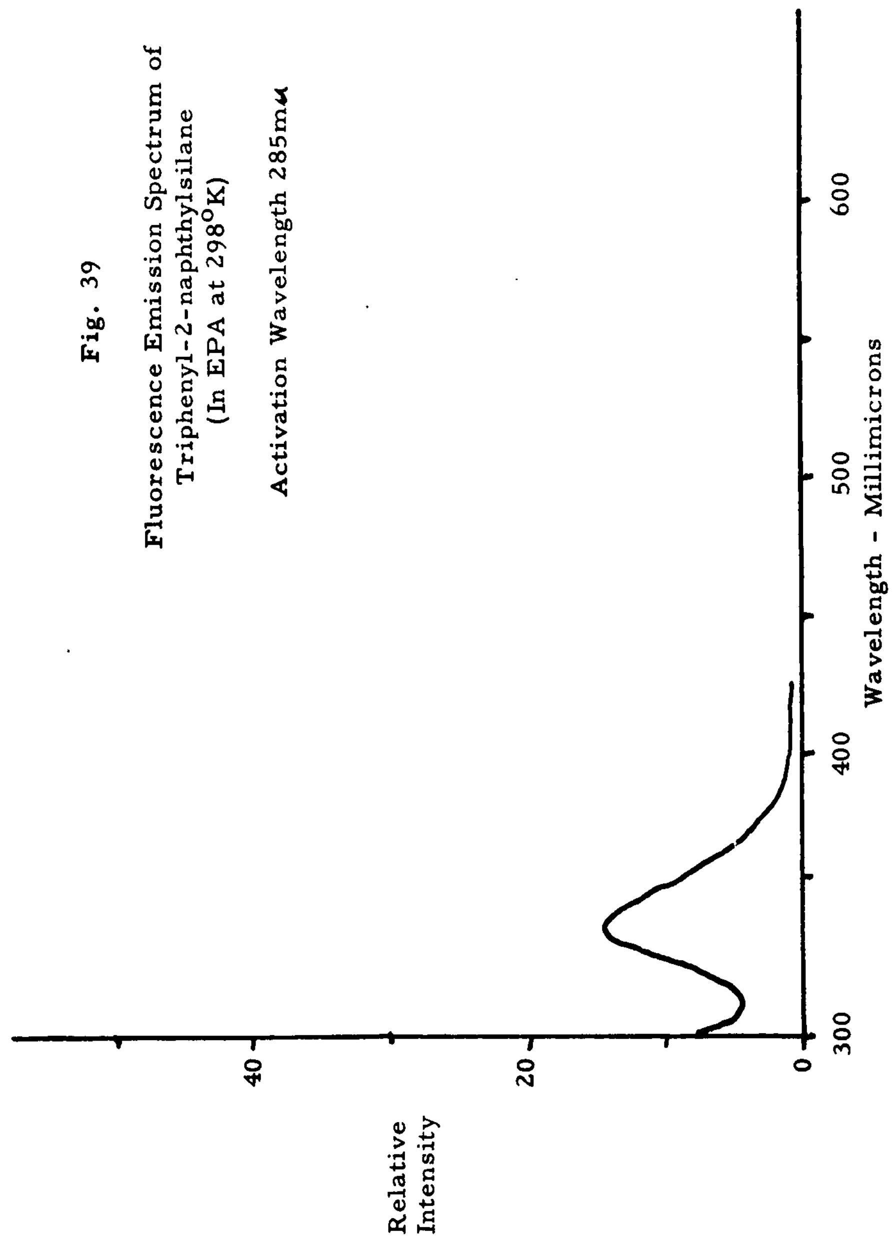


**Fig. 39**

Fluorescence Emission Spectrum of
Triphenyl-2-naphthylsilane
(In EPA at 298°K)

Activation Wavelength 285mμ

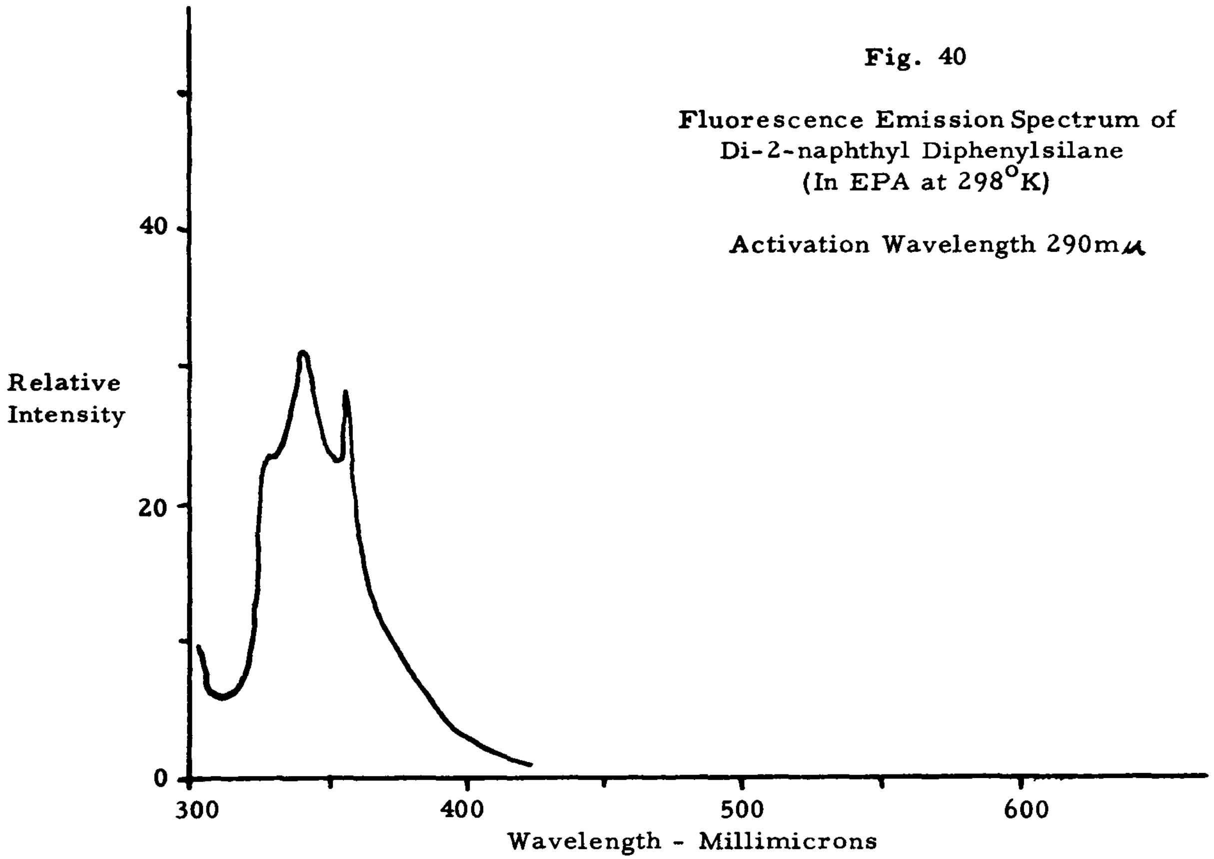


**Fig. 40**

Fluorescence Emission Spectrum of
Di-2-naphthyl Diphenylsilane
(In EPA at 298°K)

Activation Wavelength 290mμ

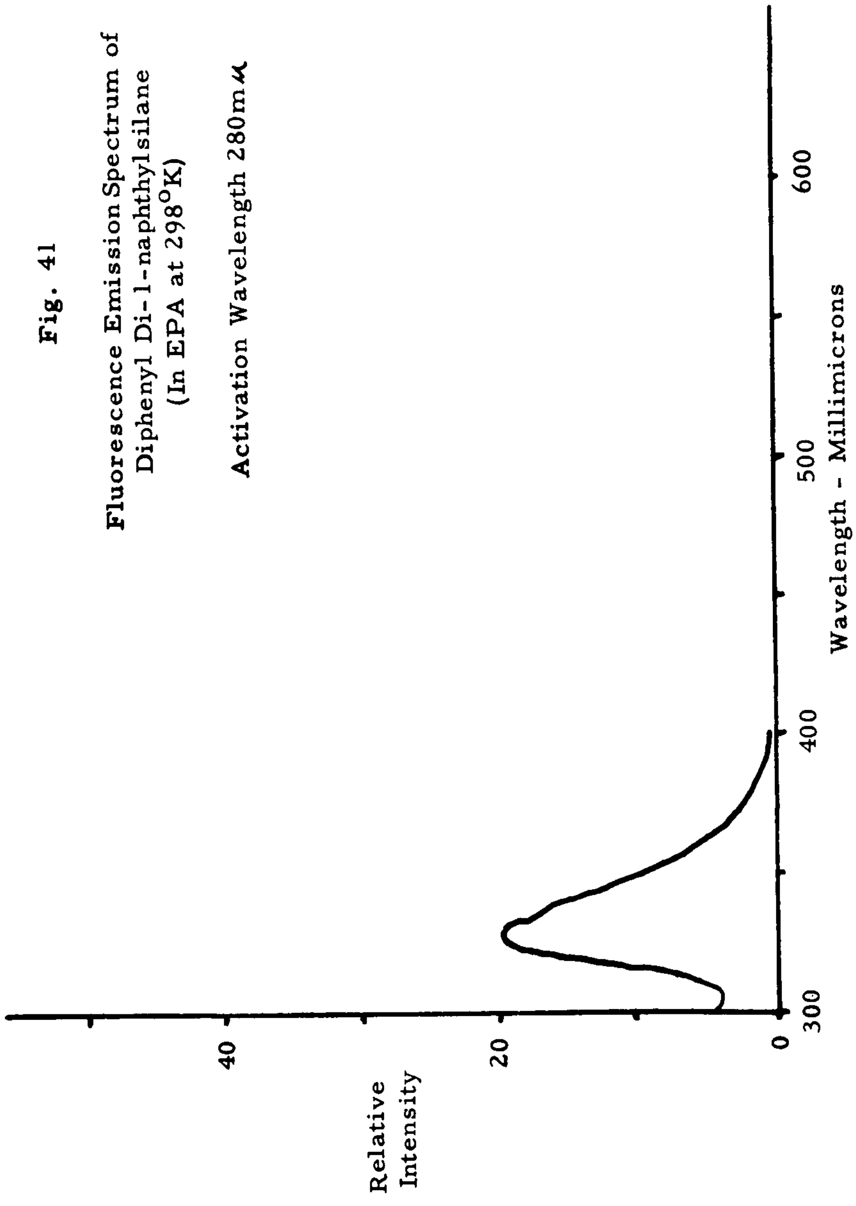


**Fig. 41**

**Fluorescence Emission Spectrum of Diphenyl Di-1-naphthylsilane (In EPA at 298°K)**

**Activation Wavelength 280 mμ**

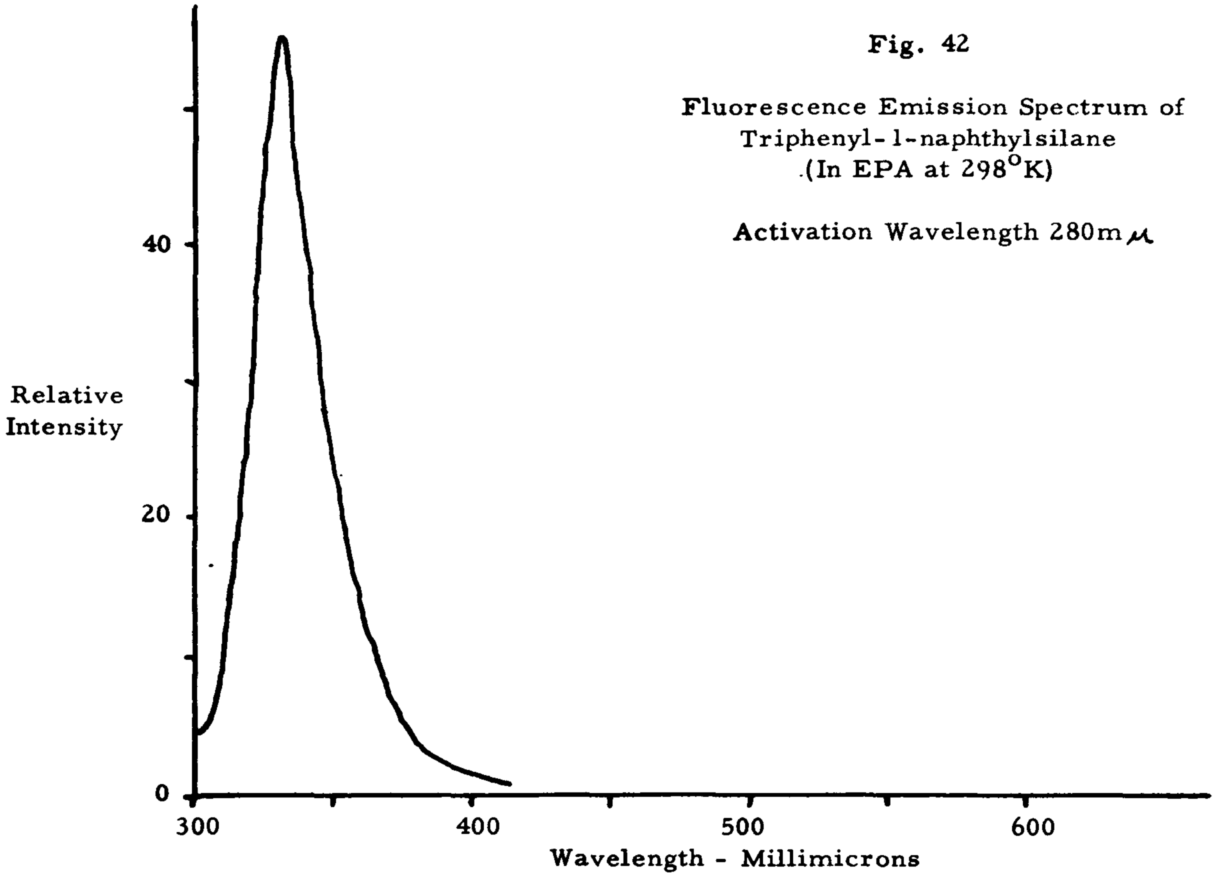


Fig. 42

Fluorescence Emission Spectrum of
Triphenyl-1-naphthylsilane
(In EPA at 298°K)

Activation Wavelength 280m$\mu$

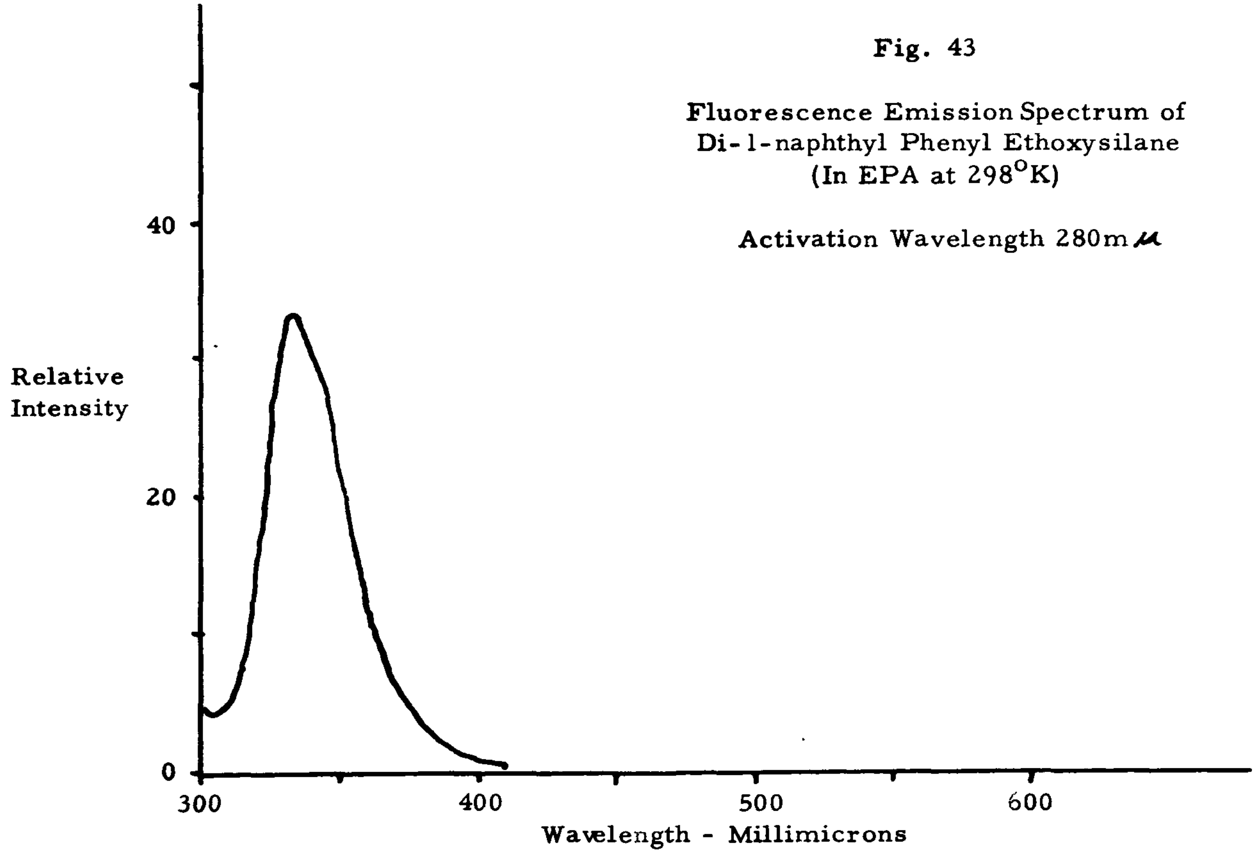


Fig. 43

Fluorescence Emission Spectrum of
Di-1-naphthyl Phenyl Ethoxysilane
(In EPA at 298°K)

Activation Wavelength 280m$\mu$

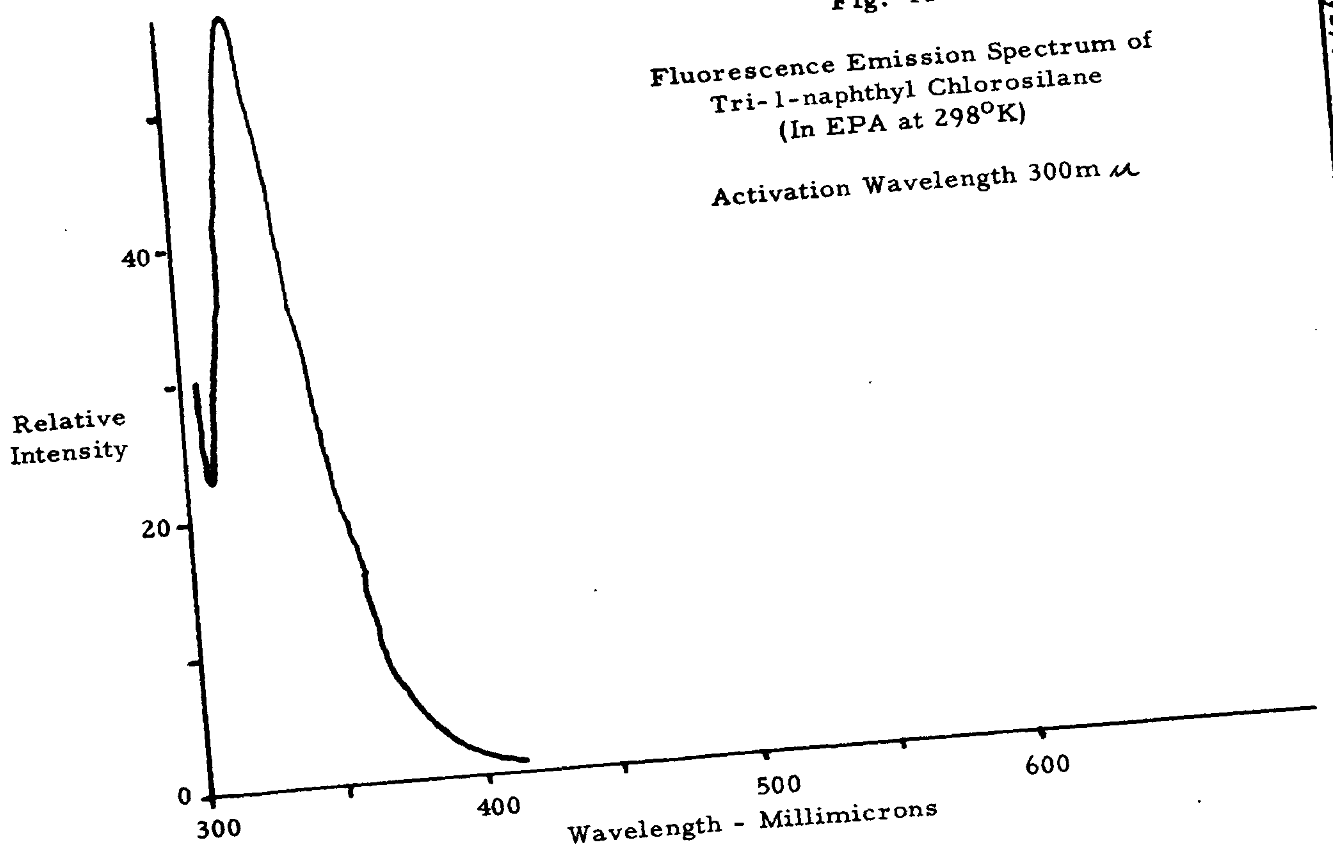


Fig. 44

Fluorescence Emission Spectrum of
Tri-1-naphthyl Chlorosilane
(In EPA at 298°K)

Activation Wavelength 300m$\mu$

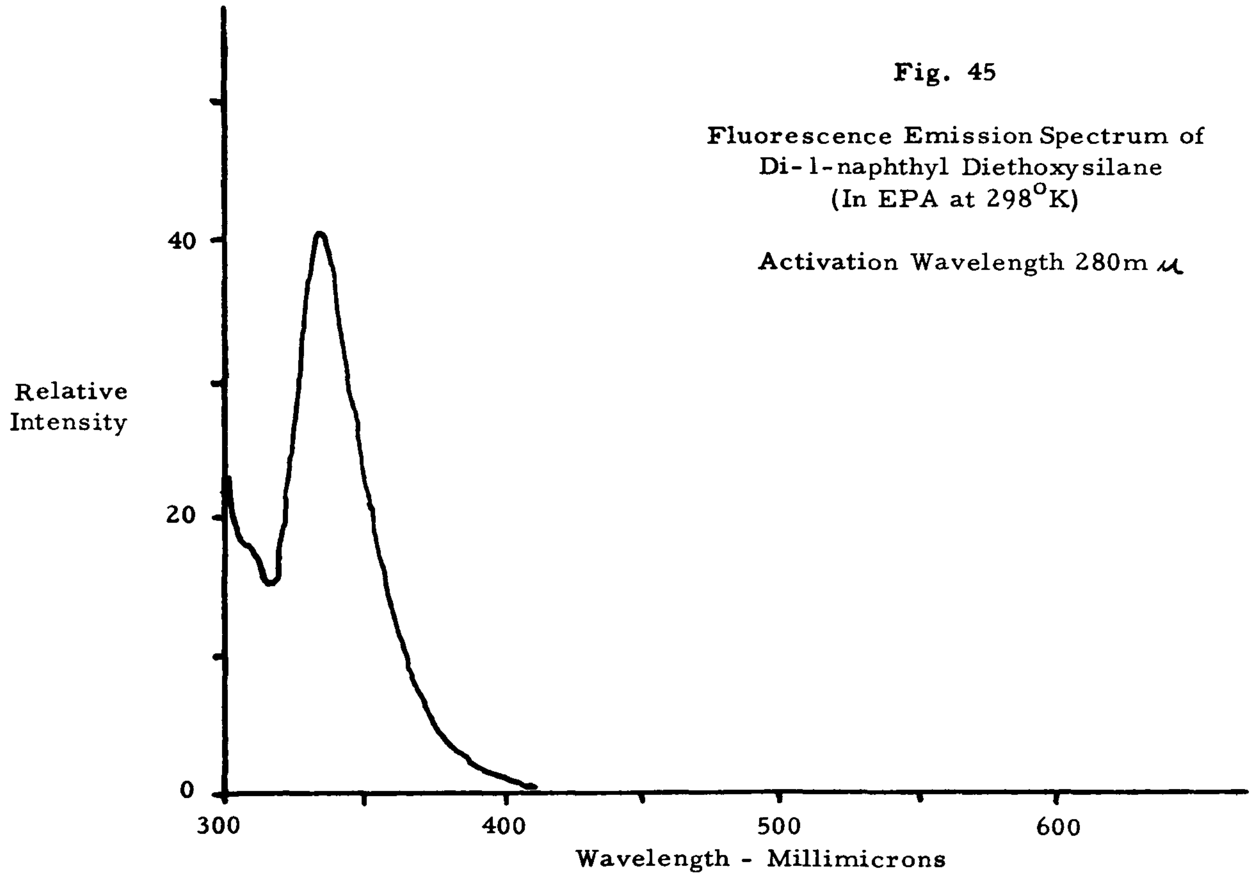


Fig. 45

Fluorescence Emission Spectrum of
Di-1-naphthyl Diethoxysilane
(In EPA at 298°K)

Activation Wavelength 280m $\mu$

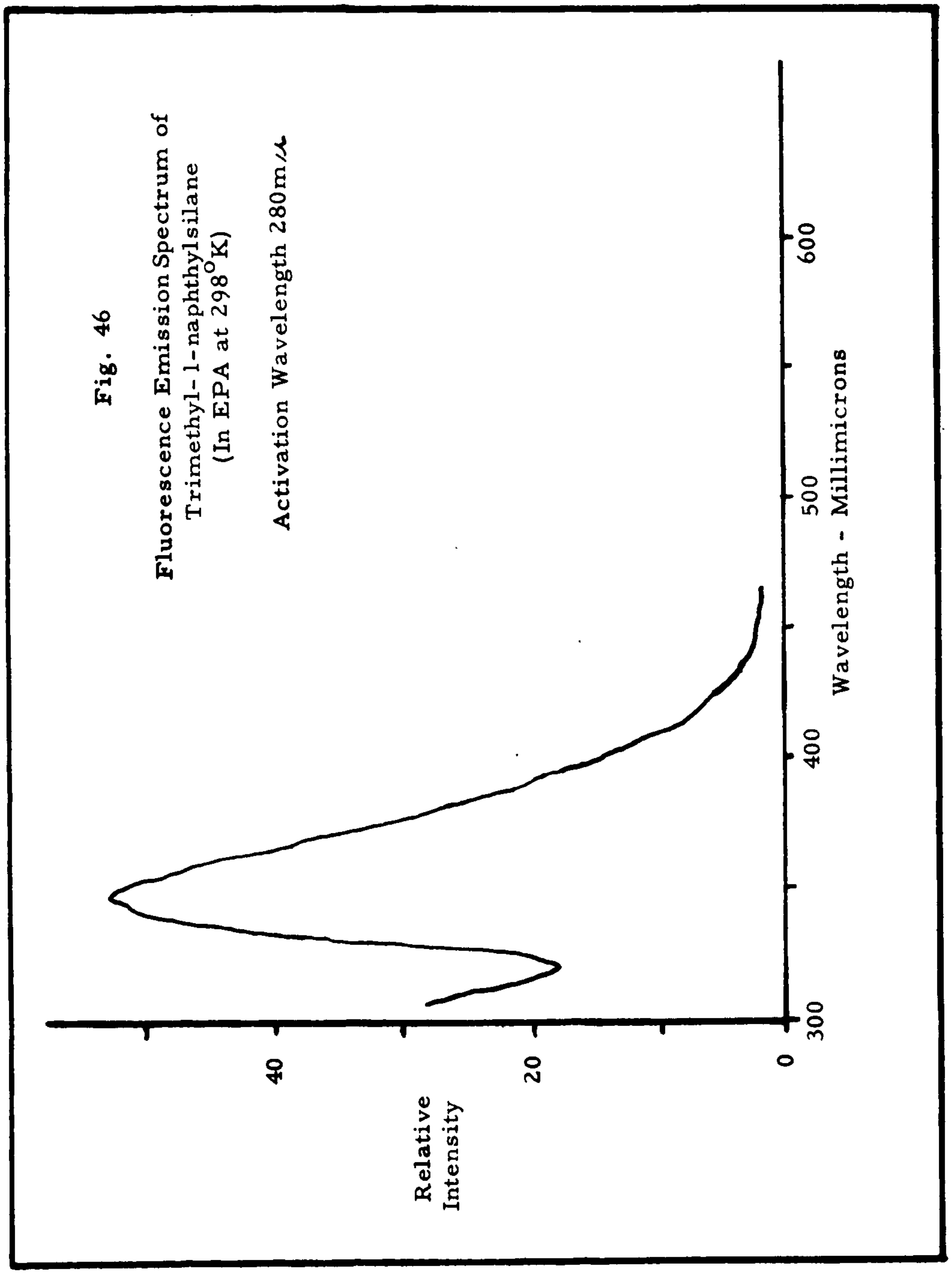


Fig. 46

**Fluorescence Emission Spectrum of**
Trimethyl-1-naphthylsilane
(In EPA at 298°K)

Activation Wavelength 280mμ

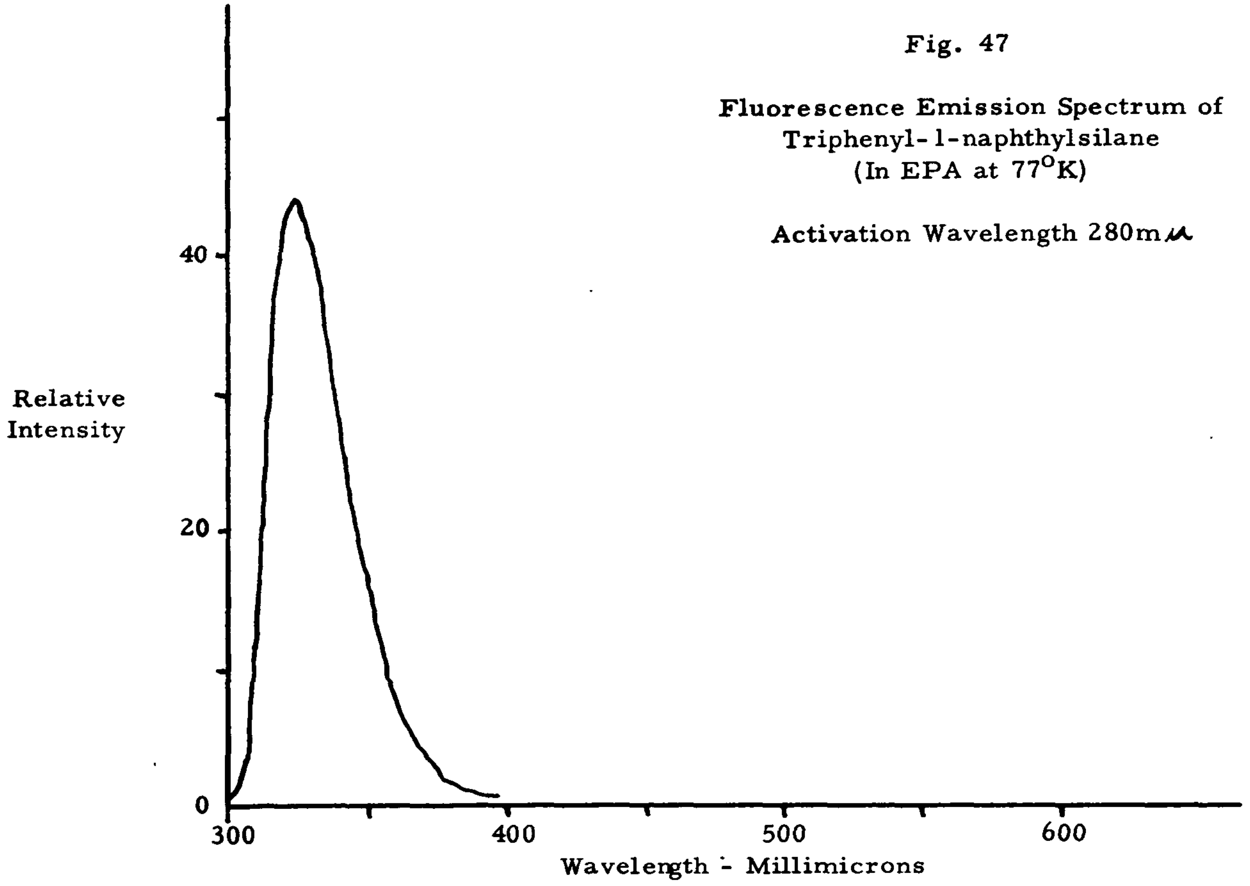


Fig. 47

Fluorescence Emission Spectrum of
Triphenyl-1-naphthylsilane
(In EPA at 77°K)

Activation Wavelength 280mμ

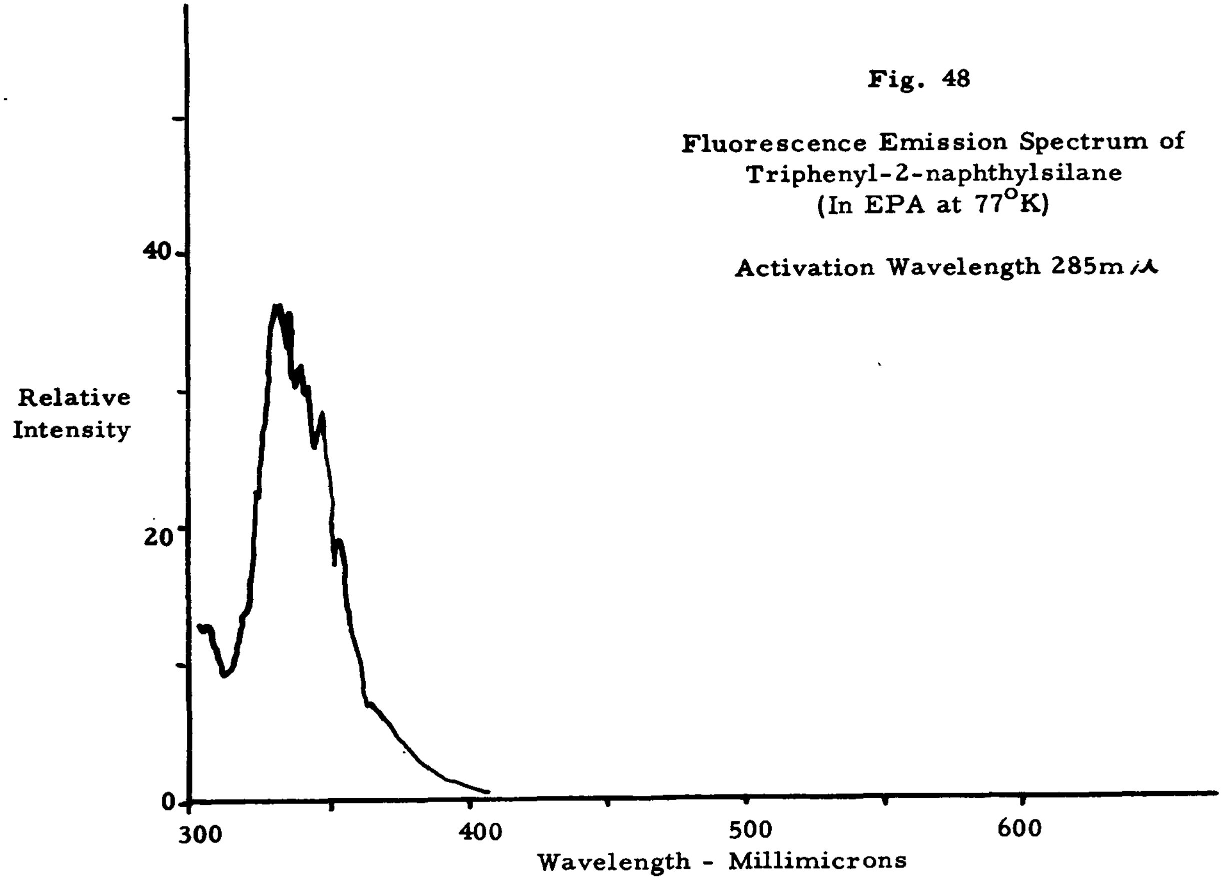


Fig. 48

Fluorescence Emission Spectrum of
Triphenyl-2-naphthylsilane
(In EPA at 77°K)

Activation Wavelength 285m$\mu$

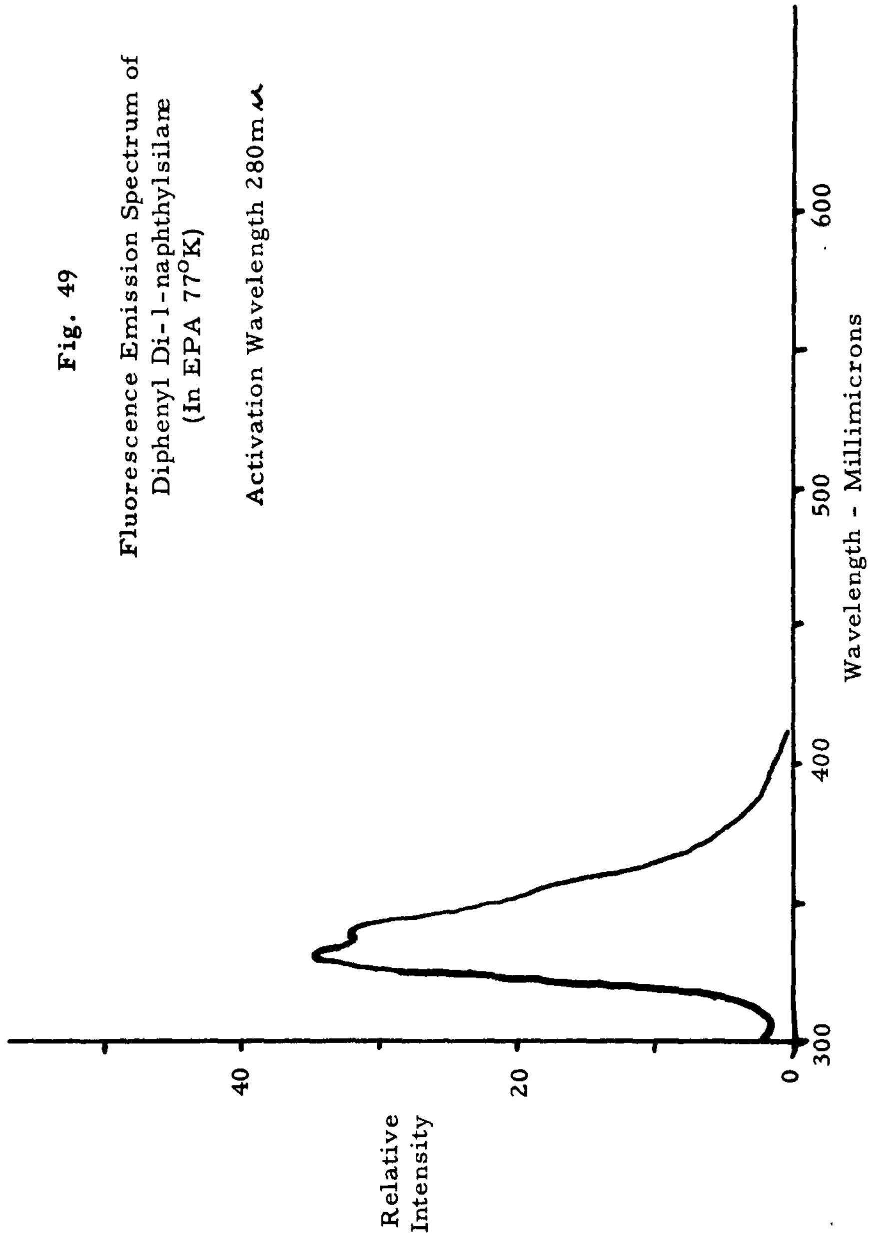


Fig. 49

Fluorescence Emission Spectrum of Diphenyl Di-1-naphthylsilane (In EPA 77°K)

Activation Wavelength 280mμ

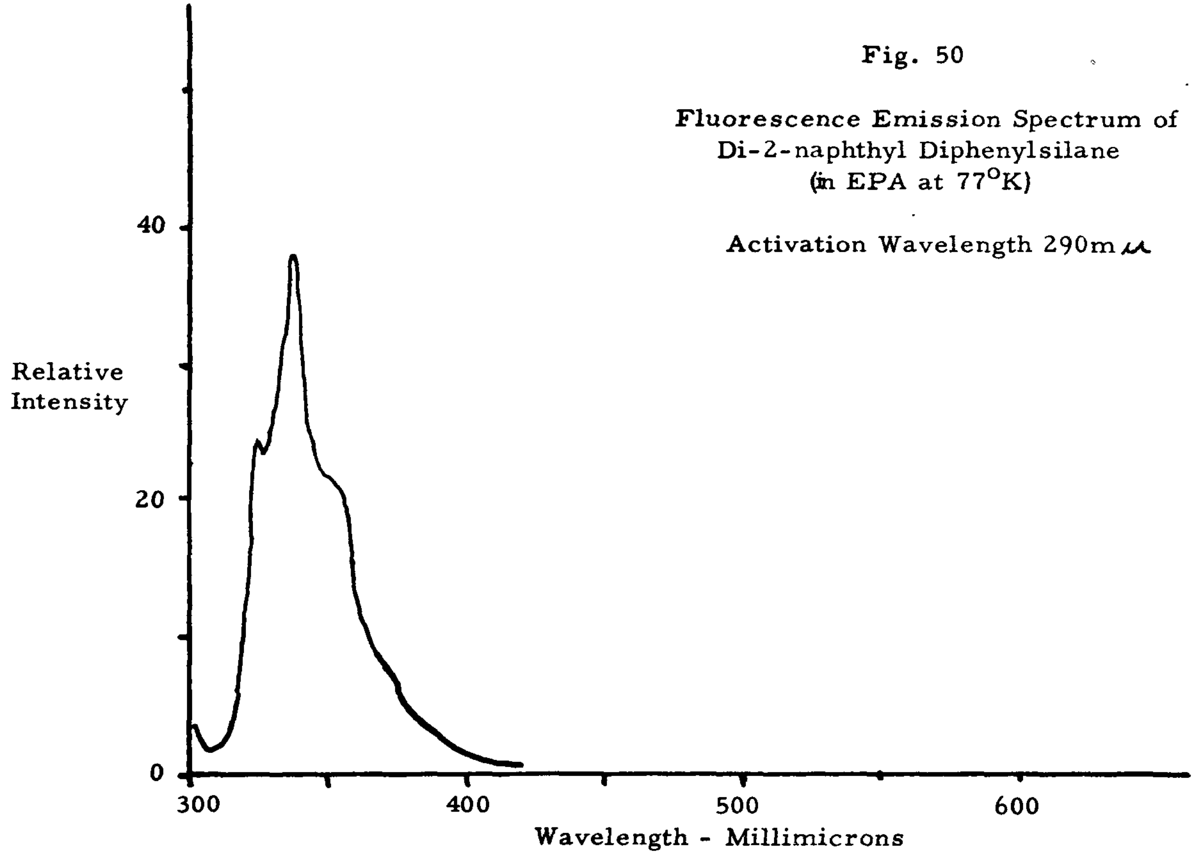


Fig. 50

Fluorescence Emission Spectrum of
Di-2-naphthyl Diphenylsilane
(in EPA at 77$^{\circ}$K)

Activation Wavelength 290m$\mu$

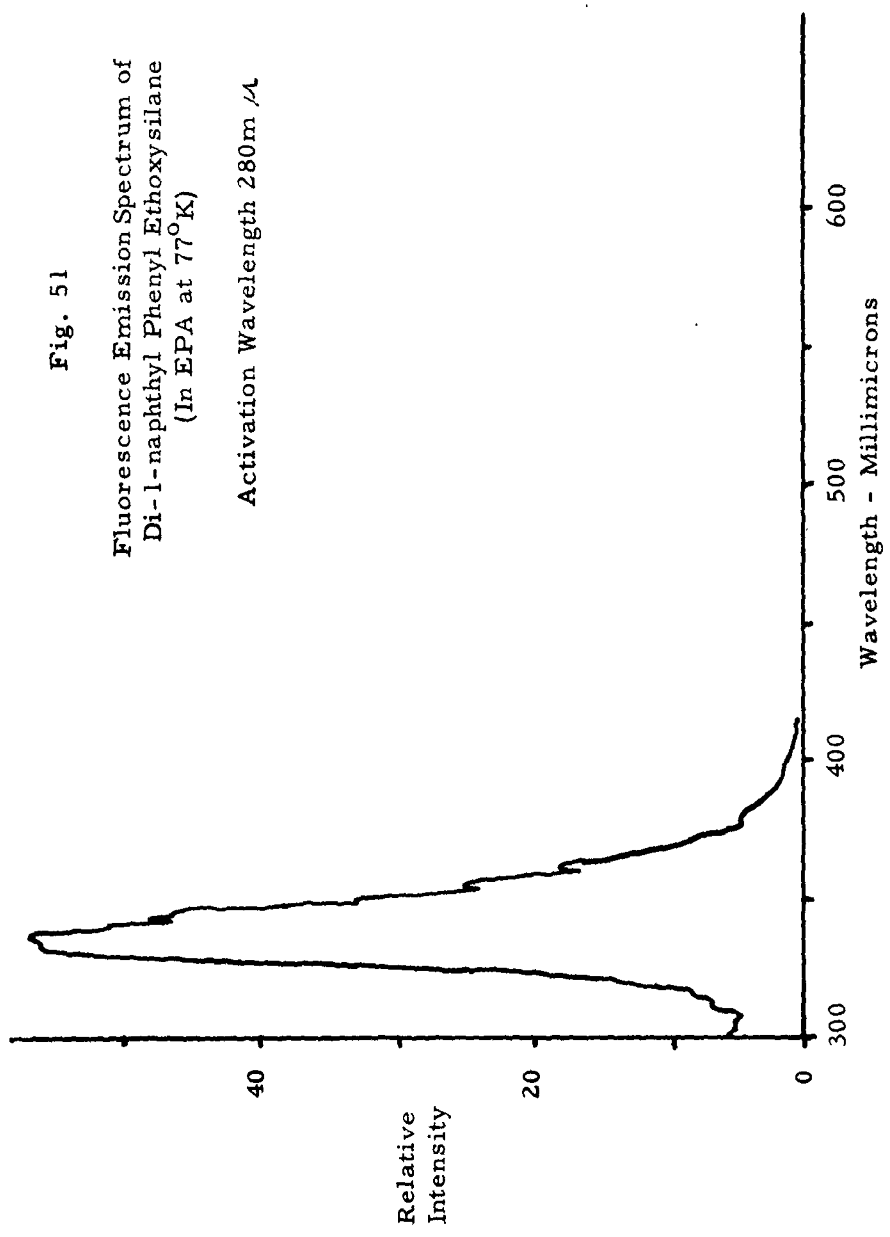


Fig. 51

Fluorescence Emission Spectrum of Di-1-naphthyl Phenyl Ethoxysilane (In EPA at 77°K)

Activation Wavelength 280m $\mu$

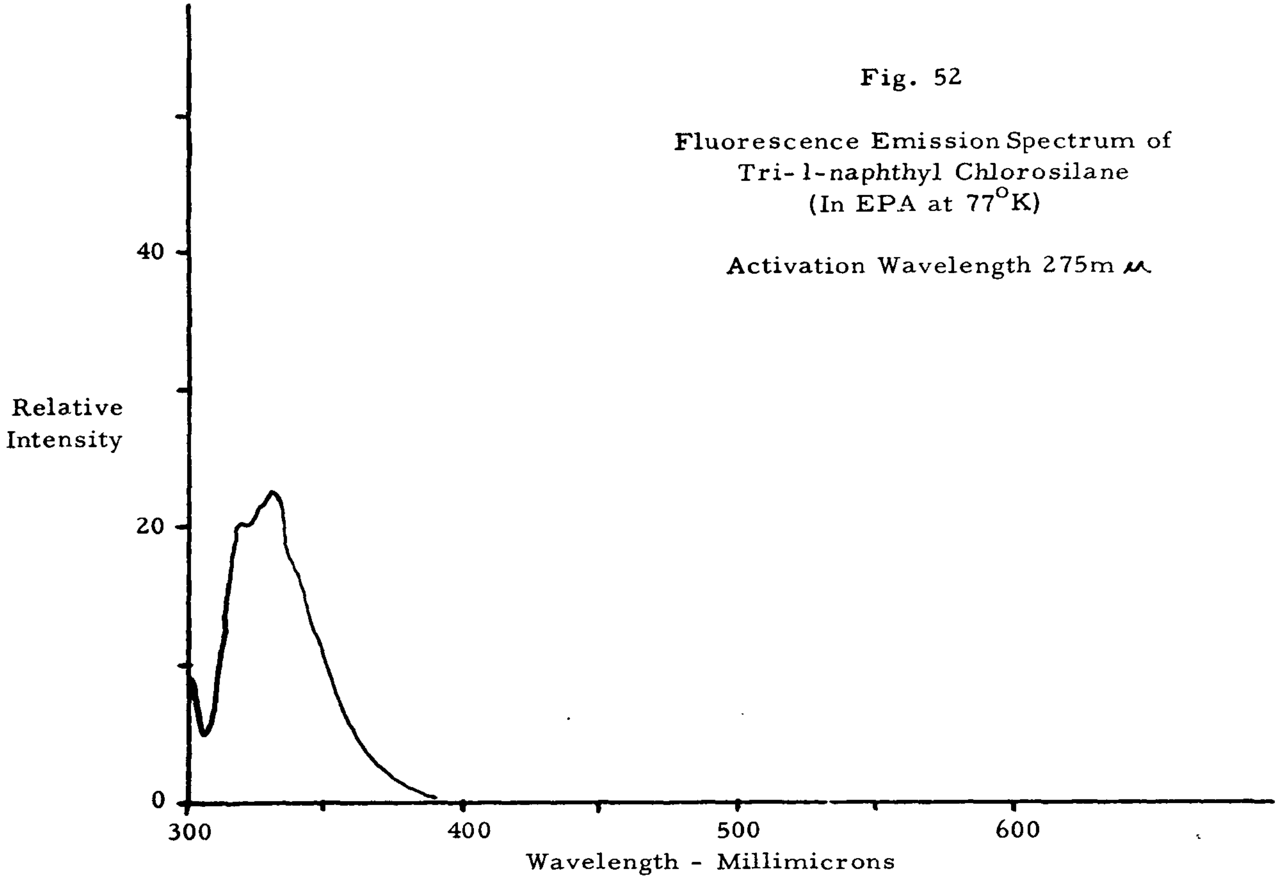


Fig. 52

Fluorescence Emission Spectrum of
Tri-1-naphthyl Chlorosilane
(In EPA at 77°K)

Activation Wavelength 275m μ

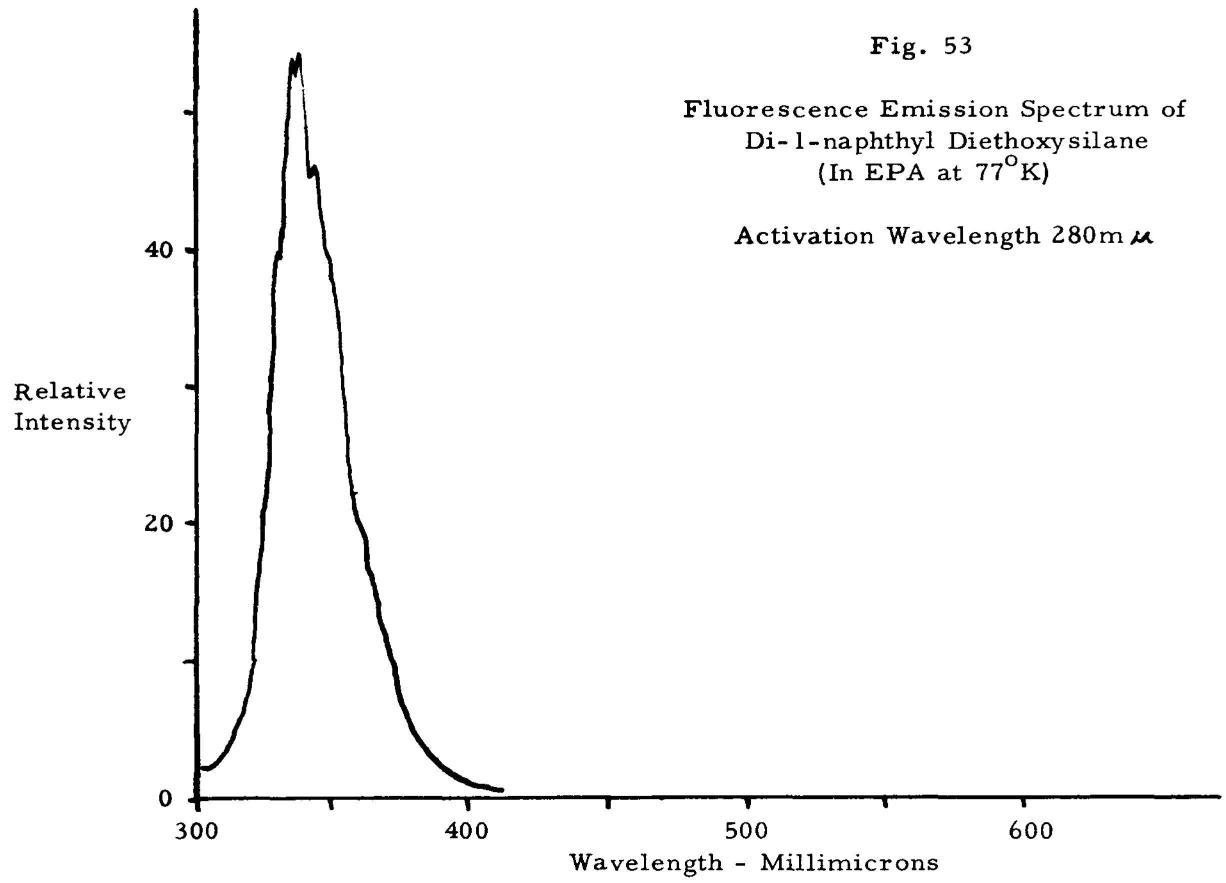


Fig. 53

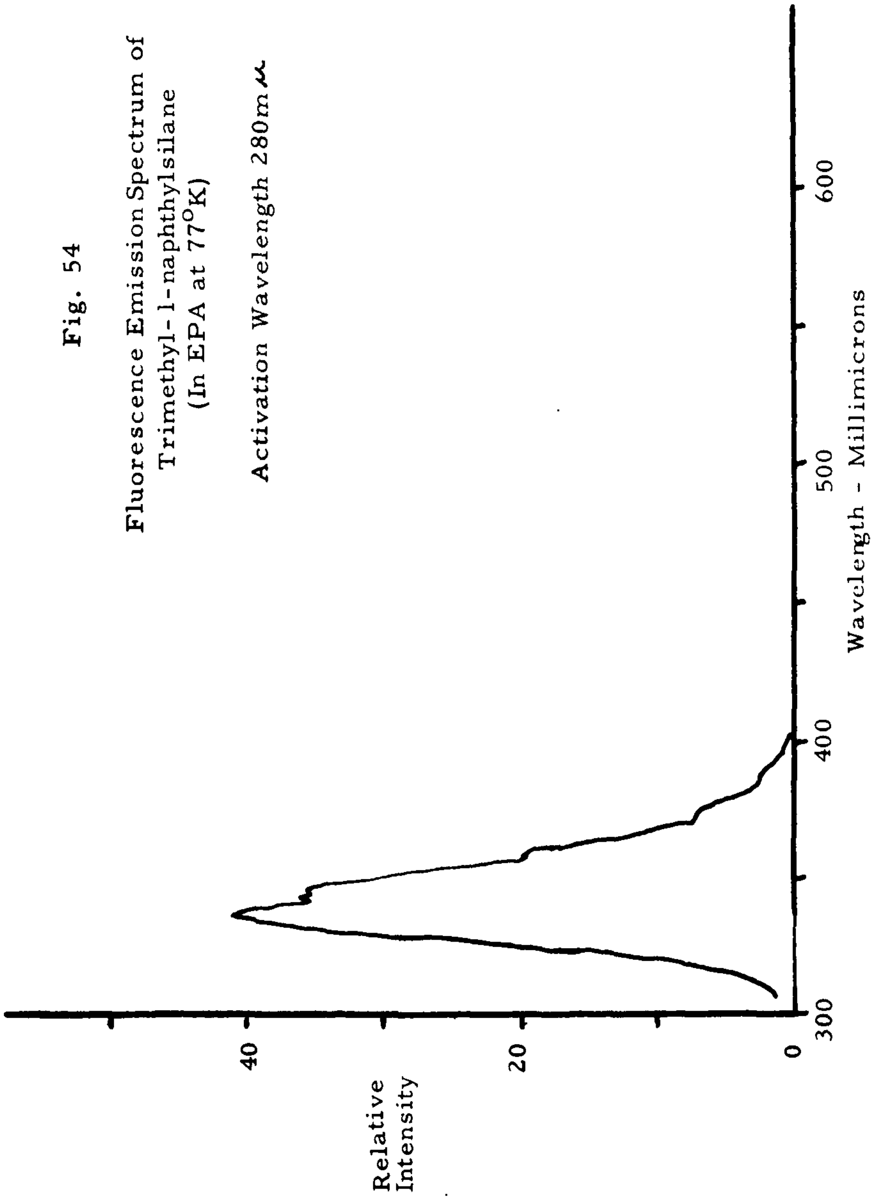
Fluorescence Emission Spectrum of
Di-1-naphthyl Diethoxysilane
(In EPA at 77°K)

Activation Wavelength 280mμ

**Fig. 54**

Fluorescence Emission Spectrum of
Trimethyl-1-naphthylsilane
(In EPA at 77°K)

Activation Wavelength 280 mμ



# Appendix C

## Phosphorescent Emission Spectra of Naphthyl Silanes

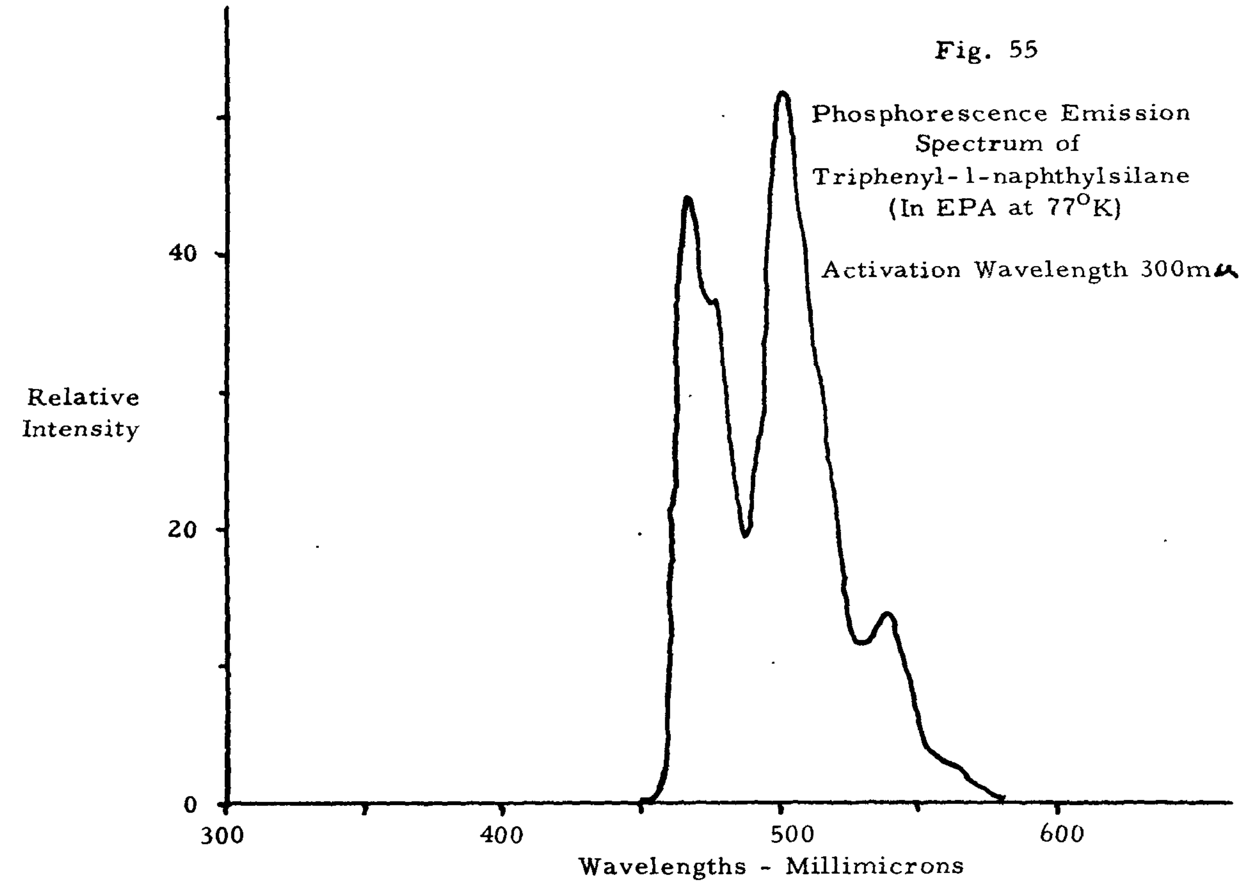


Fig. 55

Phosphorescence Emission
Spectrum of
Triphenyl-1-naphthylsilane
(In EPA at 77$^{\circ}$K)

Activation Wavelength 300m$\mu$

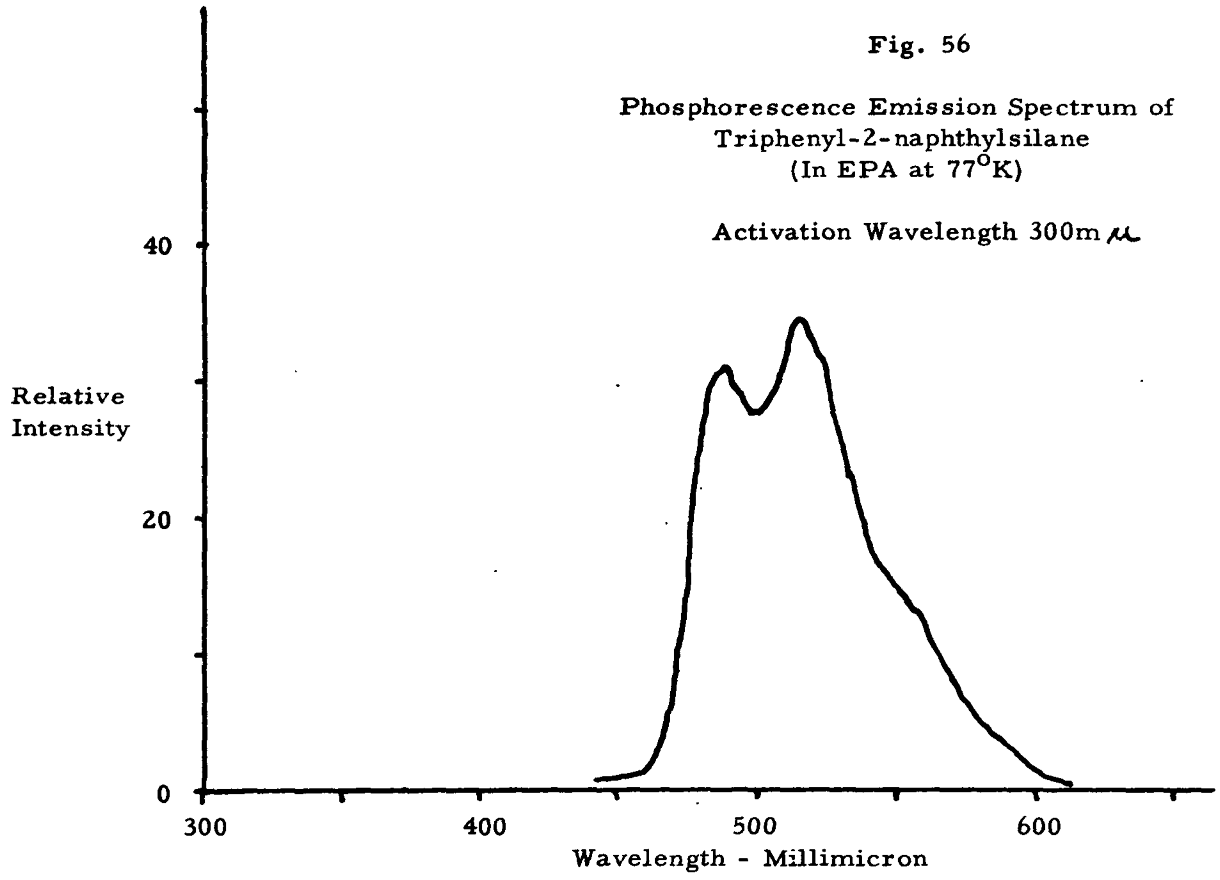


Fig. 56

Phosphorescence Emission Spectrum of
Triphenyl-2-naphthylsilane
(In EPA at 77$^{\circ}$K)

Activation Wavelength 300m$\mu$

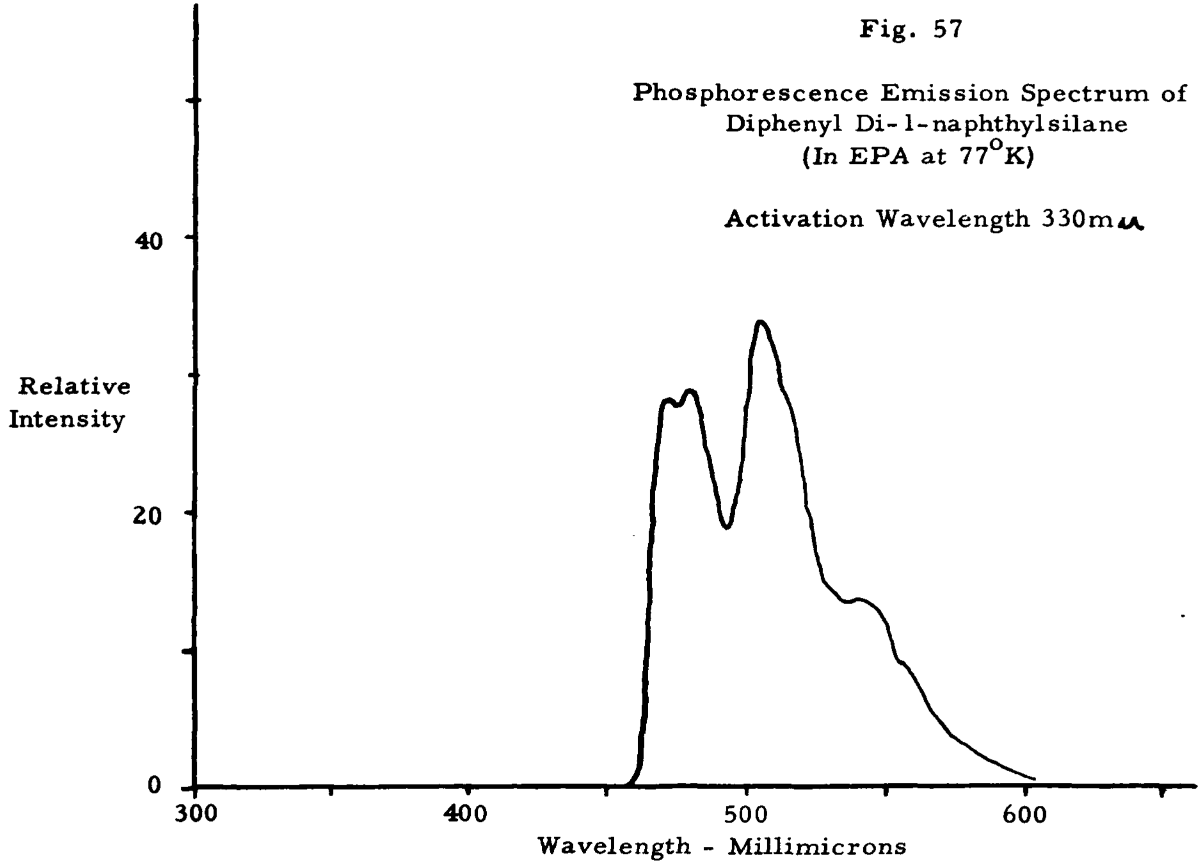


Fig. 57

Phosphorescence Emission Spectrum of Diphenyl Di-1-naphthylsilane (In EPA at 77°K)

Activation Wavelength 330m$\mu$

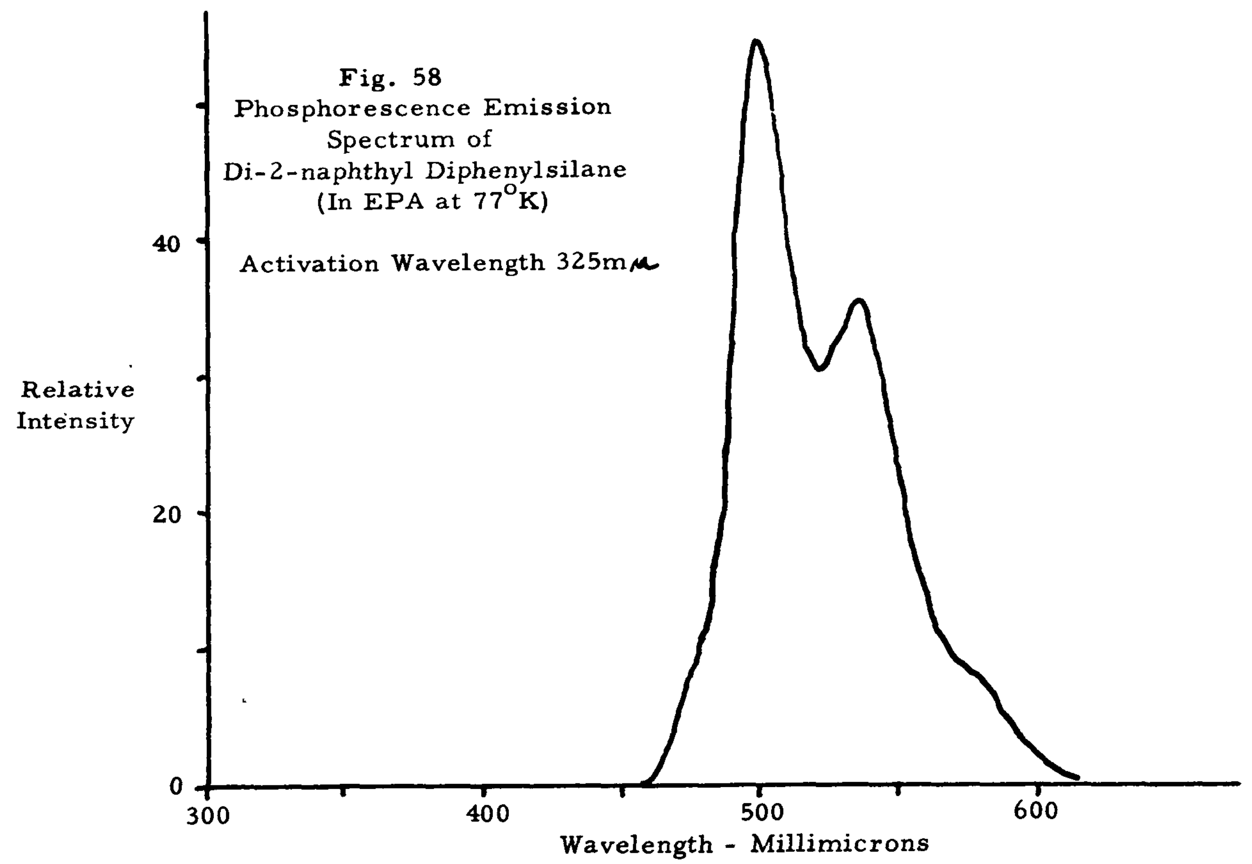


Fig. 58
Phosphorescence Emission
Spectrum of
Di-2-naphthyl Diphenylsilane
(In EPA at 77$^\circ$K)

Activation Wavelength 325mμ

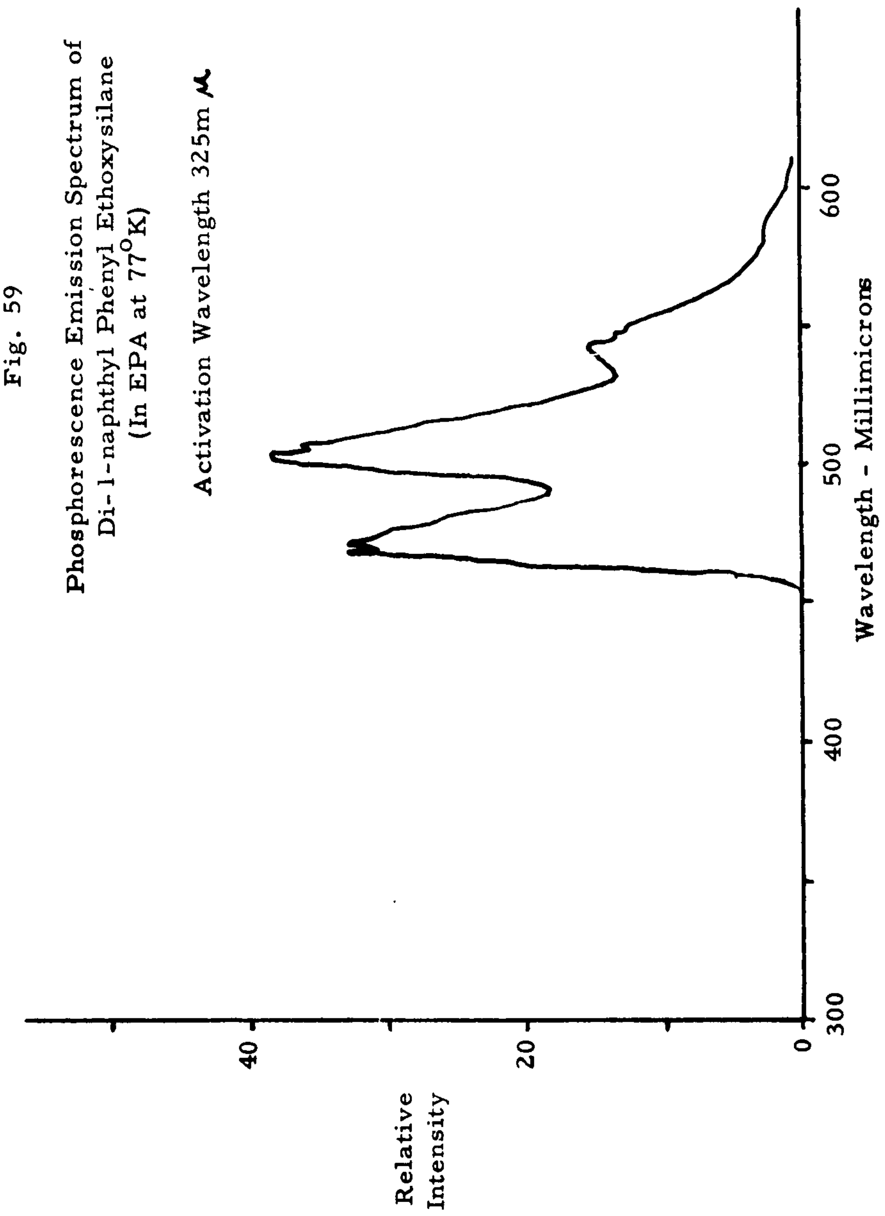


Fig. 59

Phosphorescence Emission Spectrum of Di-1-naphthyl Phenyl Ethoxysilane (In EPA at 77$^{\circ}$K)

Activation Wavelength 325m $\mu$

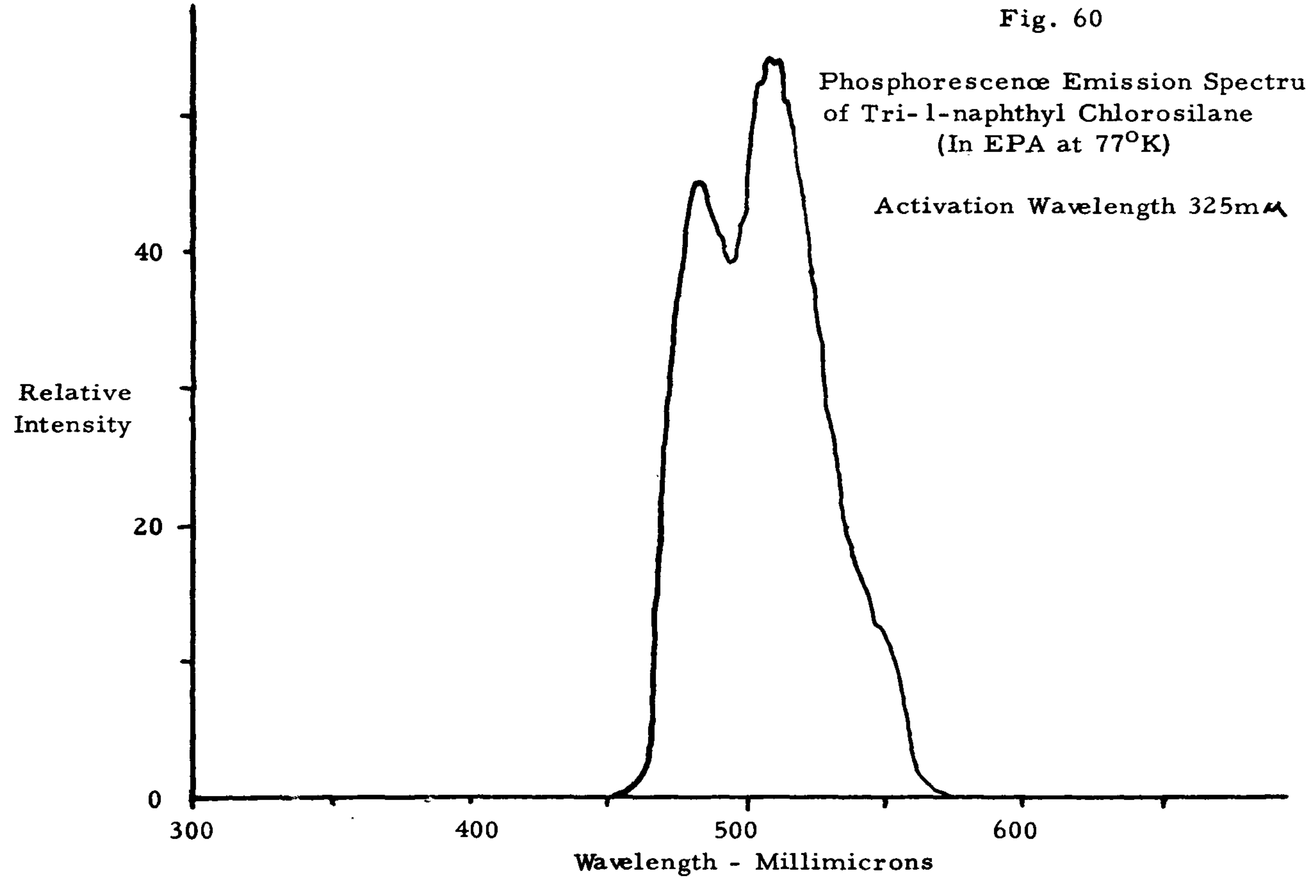


Fig. 60

Phosphorescence Emission Spectrum of Tri-1-naphthyl Chlorosilane (In EPA at 77°K)

Activation Wavelength 325mμ

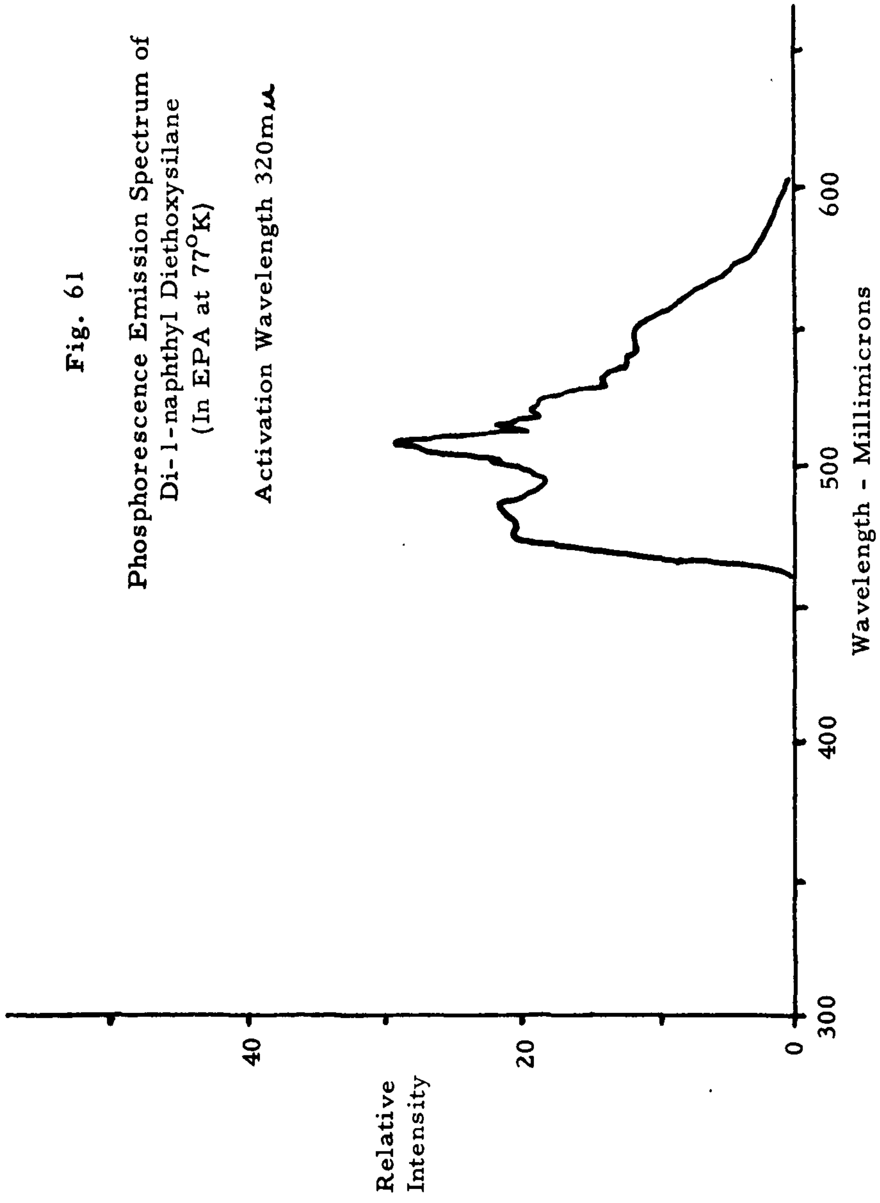


Fig. 61

Phosphorescence Emission Spectrum of
Di-1-naphthyl Diethoxysilane
(In EPA at 77°K)

Activation Wavelength 320mμ

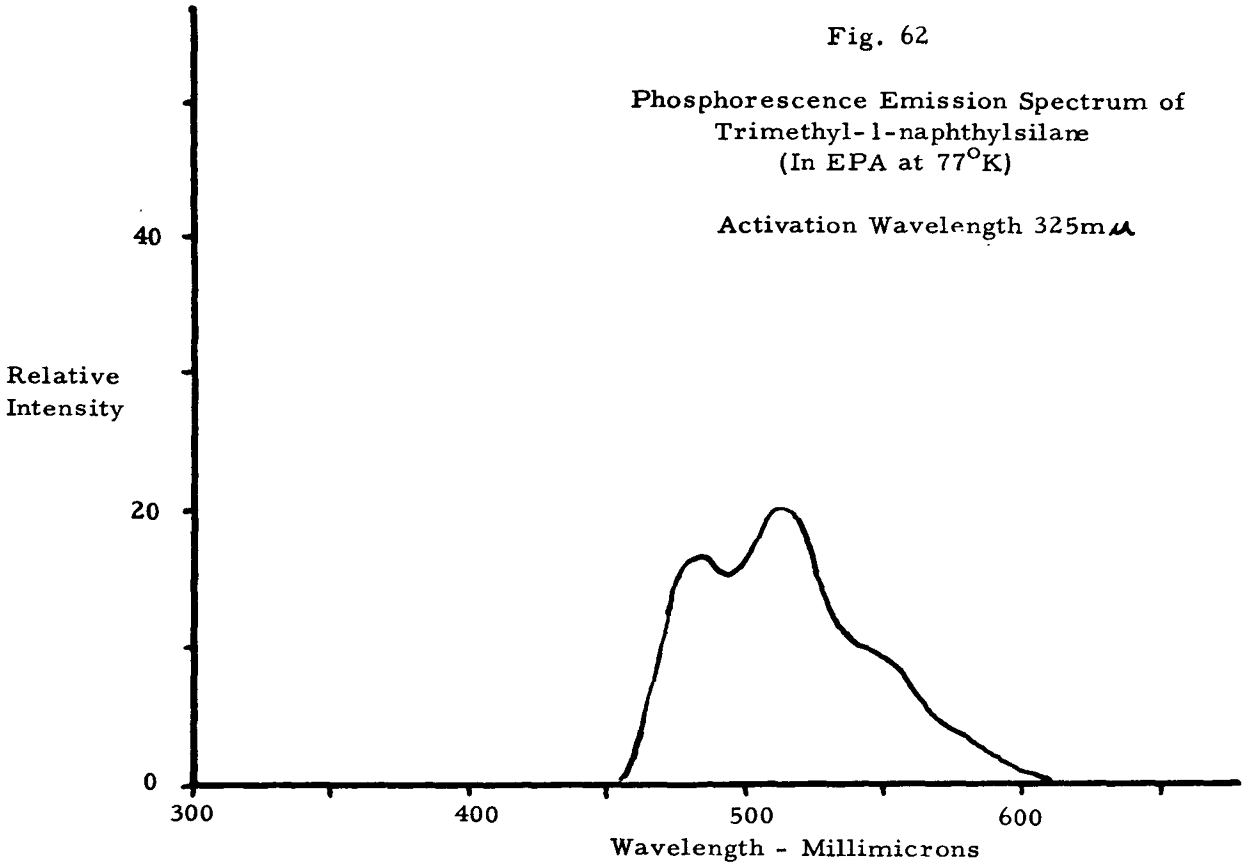


Fig. 62

Phosphorescence Emission Spectrum of
Trimethyl-1-naphthylsilane
(In EPA at 77°K)

Activation Wavelength 325mμ

# Appendix D

## Naphthalene and Indole Emission Spectra and Correction Curves

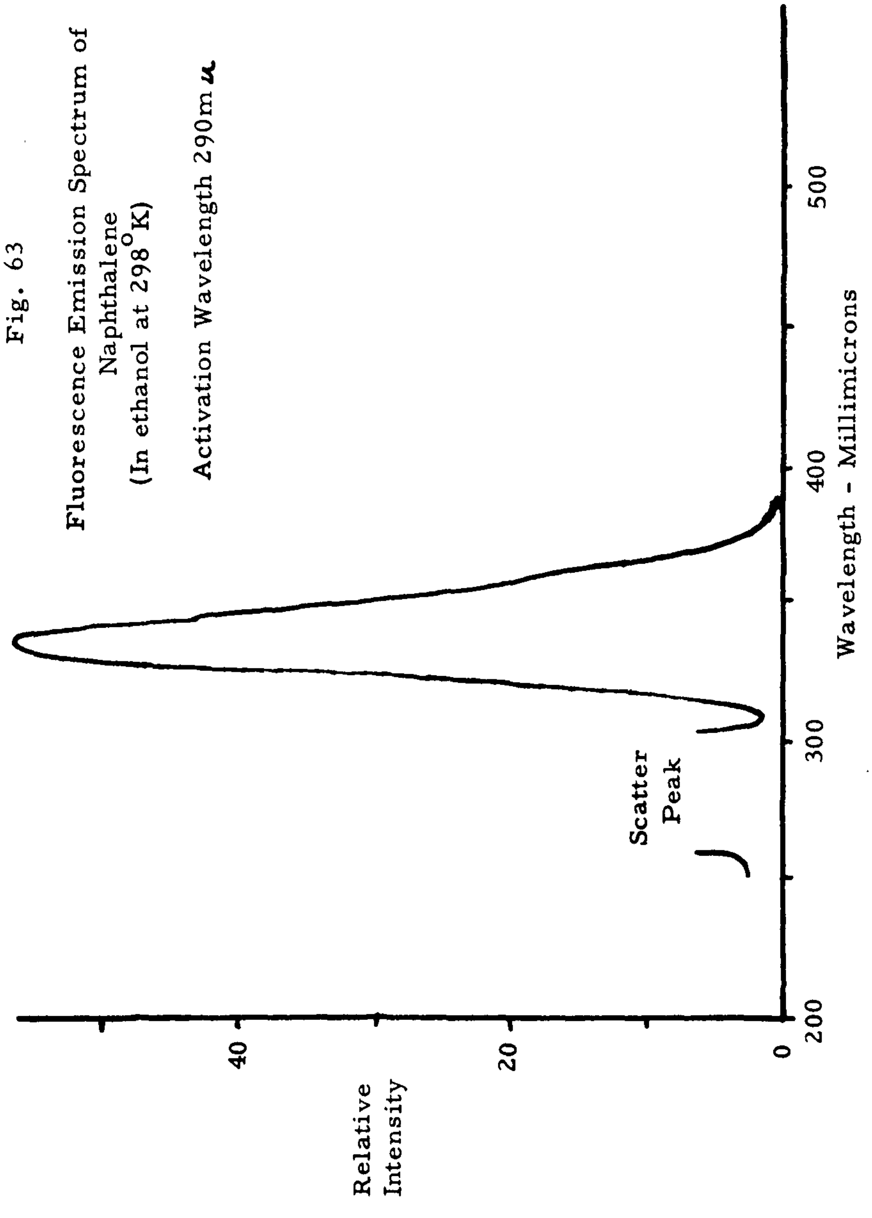


Fig. 63

Fluorescence Emission Spectrum of Naphthalene
(In ethanol at 298°K)

Activation Wavelength 290mμ

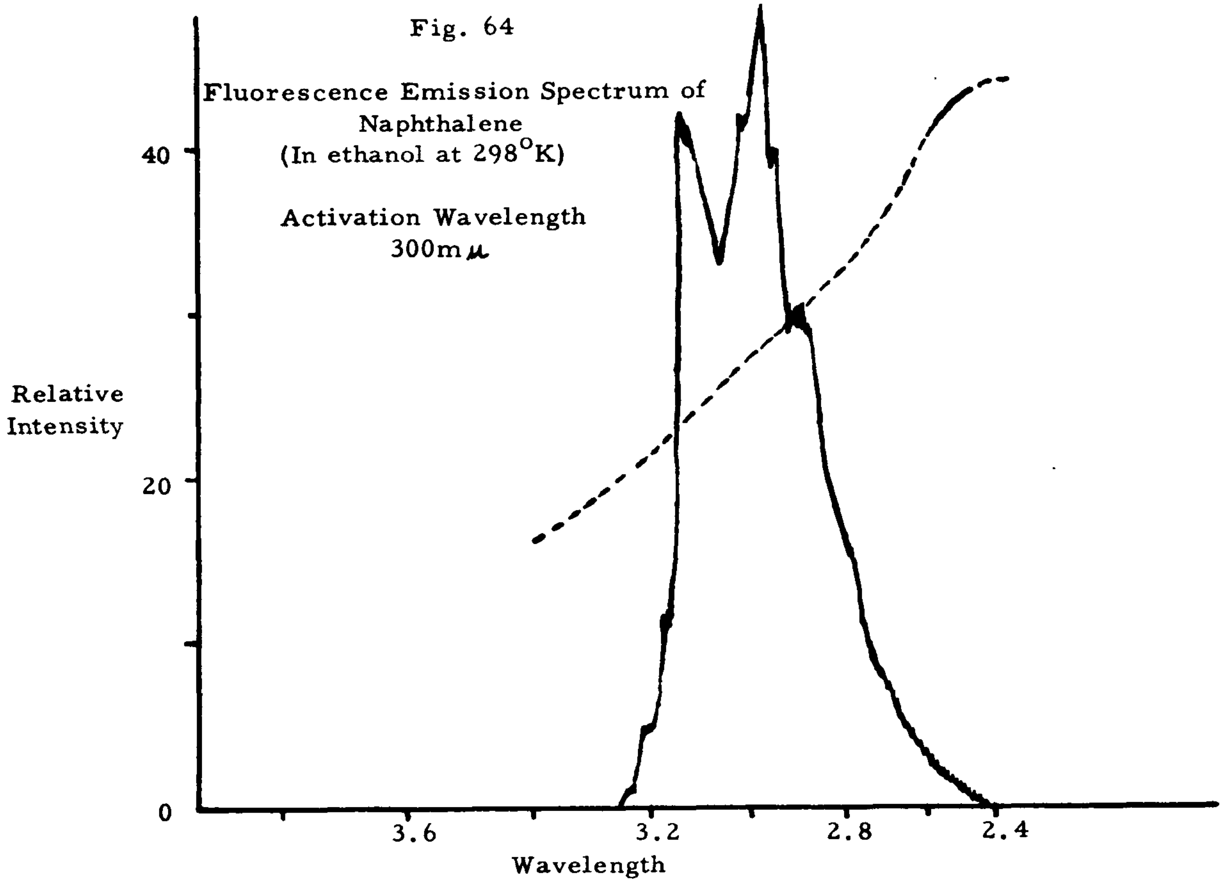


Fig. 64

Fluorescence Emission Spectrum of Naphthalene (In ethanol at 298°K)

Activation Wavelength 300mμ

----- Sensitivity of quartz monochromator with E.M.I. 6256 photomultiplier. (Ref14:103)

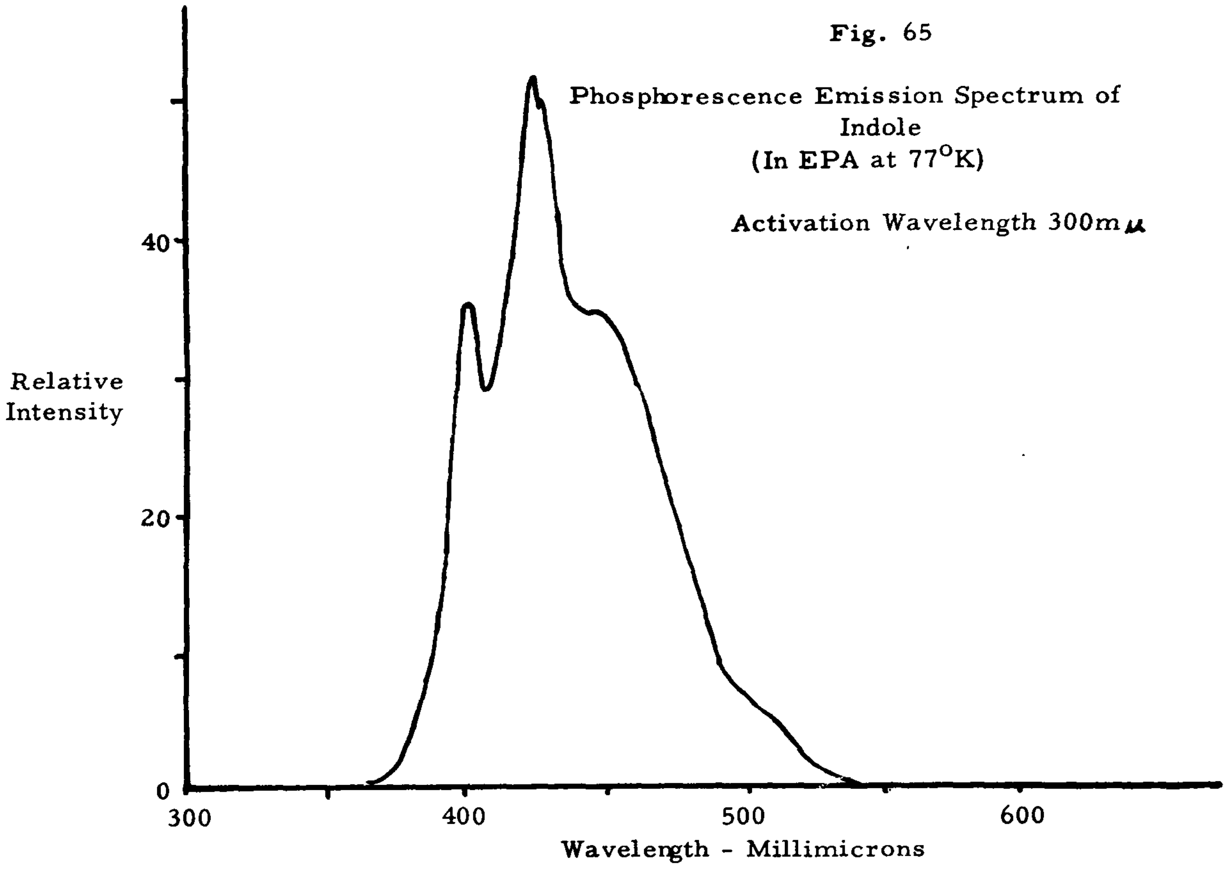


**Fig. 65**

Phosphorescence Emission Spectrum of
Indole
(In EPA at 77$^{\circ}$K)

Activation Wavelength 300m$\mu$

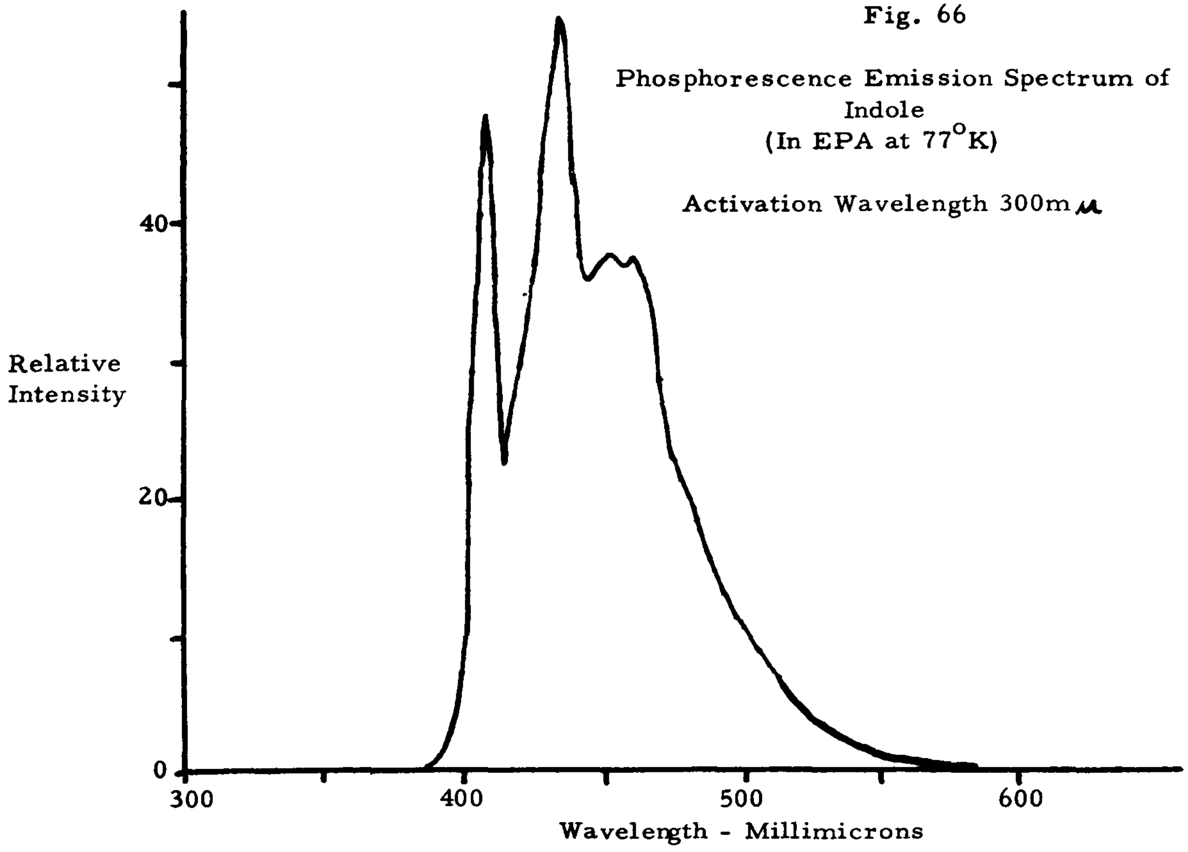


Fig. 66

Phosphorescence Emission Spectrum of Indole
(In EPA at 77°K)

Activation Wavelength 300m$\mu$

(Ref 2:11)

# Appendix E

## Sample Curves For Calculating Mean Phosphorescent Lifetimes

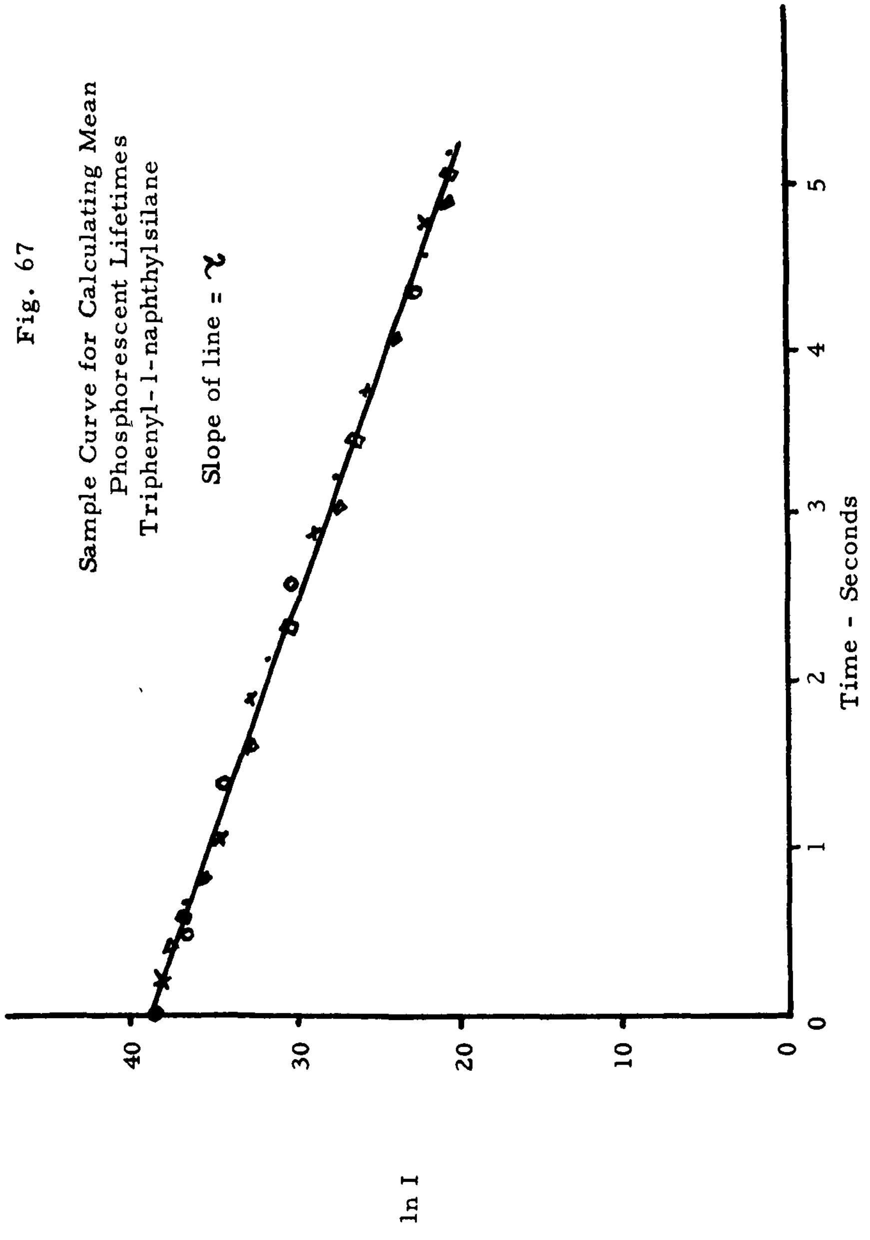


Fig. 67

Sample Curve for Calculating Mean Phosphorescent Lifetimes Triphenyl-1-naphthylsilane

Slope of line = $\tau$

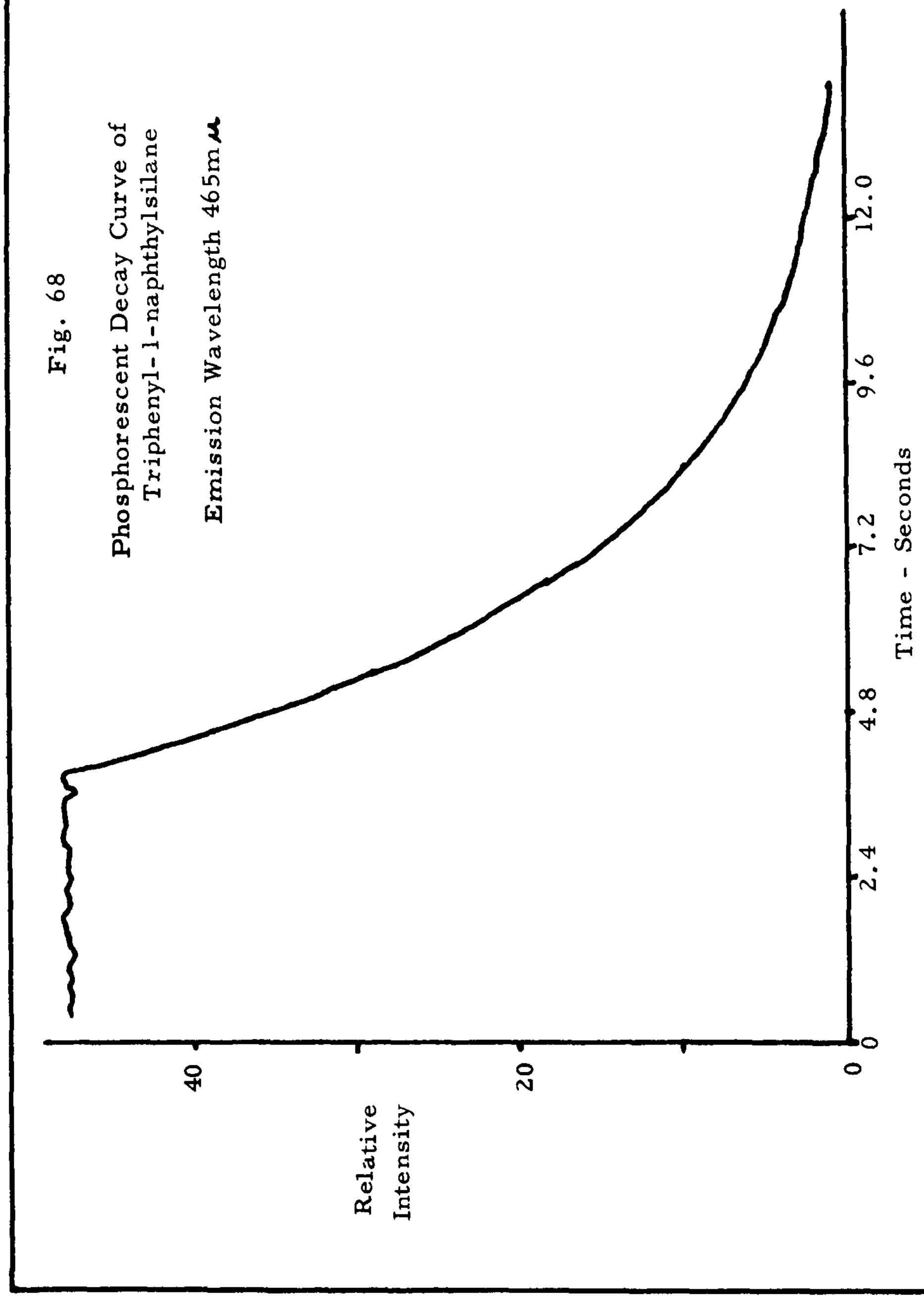


Fig. 68

Phosphorescent Decay Curve of Triphenyl-1-naphthylsilane

Emission Wavelength 465mμ