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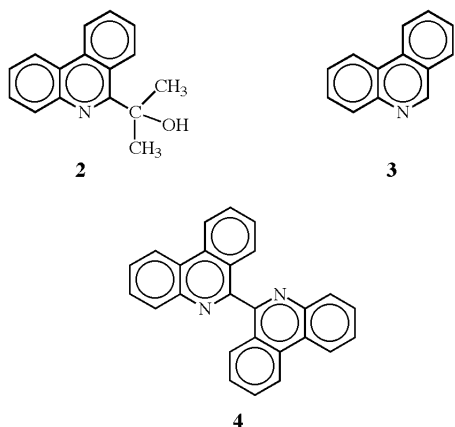
Received April 4, 2000

The physical and photophysical properties of 6-phenanthridinecarbonitrile (**1**) have been examined. We previously reported that when **1** is irradiated in aqueous 2-propanol, three products are formed [3]. These include dimethyl-6-phenanthridinylcarbinol (**2**), phenanthridine (**3**) and 6,6'-biphenanthridine (**4**). Phenanthridinyl radical is formed in neutral media by hydrogen atom abstraction from an alcohol molecule by an excited state of **1** in a monophotonic process. The presence of acid effectively quenches all photochemical behavior. These products may all be explained assuming in-cage and out-of-cage reactions. The free spin value,  $g_{e^{\cdot}}$ , was determined at 125 K and found to be 2.0043 which is close to the theoretical value for that of a free electron. The total emission spectrum of **1** at 77 K shows a fluorescence maximum at 378 nm and a much weaker phosphorescence maximum at 502 nm which represented less than 3% of the total emission. When benzophenone is added to the reaction mixture, the triplet state of **1** is populated, but photosensitized product formation does not occur. The result supports a singlet reactive state. When *cis/trans*-piperlylene is added to the reaction mixtures, it quenches the fluorescence of **1**. The fluorescence quantum yield ( $\Phi_f$ ) was found to be 0.227 in neat 2-propanol. The addition of water causes an increase in  $\Phi_f$  and a decrease in the  $Pk_a$  of the medium. The excited state lifetime ( $\tau$ ) was determined in neat 2-propanol, using oxygen quenching, and found to be 3.4 ns. This number increased with increasing water concentration. The photoreactive state of **1** appears to be its  $\pi,\pi^*$  singlet state making its behavior more like that of the corresponding hydrocarbon parent.

*J. Heterocyclic Chem.*, **38**, 285 (2001).

### Introduction.

As a natural extension of the photochemistry of cyano pyridines and quinolines, we thought it would be interesting to examine a molecule that had an additional ring on a quinoline ring system. In the first paper of this series, we reported that the irradiation of 6-phenanthridinecarbonitrile (**1**) at 2537 Å results in the formation of compounds **2**, **3** and **4**. We would now like to present the physical and photophysical properties of **1** as well as further thoughts on the mechanism of the photochemical reaction.



The process of hydrogen atom abstraction has been reported as being a process that is allowed by either a singlet or a triplet  $n,\pi^*$  state. Based upon current models, the two states should exhibit comparable reactivity, though in some cases the singlet state may be considerably more

reactive due purely to energetic considerations [4]. The same model predicts, however, that for the corresponding singlet and triplets  $\pi,\pi^*$  states the process of hydrogen-atom abstraction is forbidden. Hence, the  $\pi,\pi^*$  states should be considerably less reactive than  $n,\pi^*$  states, though once again showing little difference in reactivity between the singlet and triplet states [4,5].

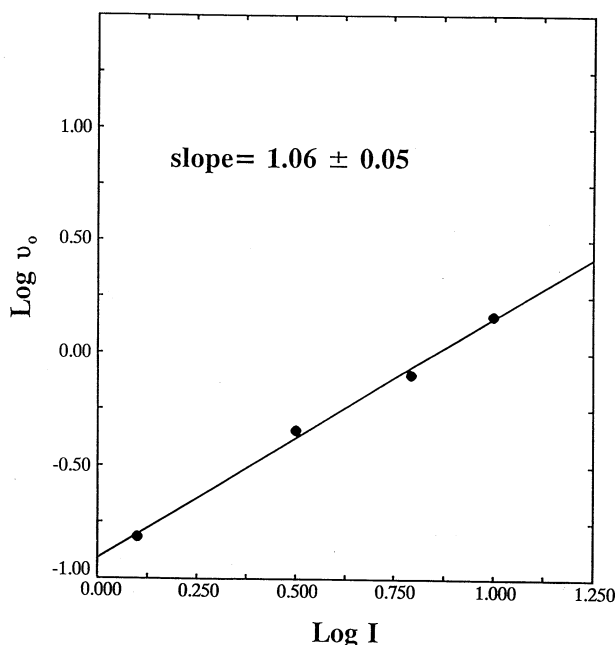


Figure 1. Kinetic plot of the Log of the Initial rate of 6-cyanophenanthridinyl radical formation ( $v_0$ ) versus the Log of the light intensity ( $I$ ).

## Results and Discussion.

The 6-cyanophenanthridinyl radical is formed by a monophotonic process (Figure 1) and since the photochemistry of **1** is believed to involve hydrogen atom abstraction, it was now necessary to determine whether the lowest excited state was either  $n,\pi^*$  or  $\pi,\pi$ . In addition, it was of interest to determine what effect, if any, there would be on the luminescence spectrum due to the use of aqueous 2-propanol as opposed to using neat alcohol. Luminescence measurements were performed in both polar and non-polar solvents systems at both room temperature and in liquid nitrogen in an attempt to discern which excited state is responsible for the photochemical behavior exhibited by **1**.

We found that the low temperature luminescence spectrum of **1**, in either ethanol, methanol, or 2-methylbutane, is essentially independent of solvent. All spectra exhibited both fluorescence and phosphorescence, with the phosphorescence accounting for less than 3% of the total emission area. The only real differences observed were in the shape of the individual bands of each spectrum. For example, the leading edge of the spectrum in methanol is approximately 2 nm blue-shifted with respect to that taken in 2-methylbutane. The maximum associated with the first band in each fluorescence emission is at  $279 \pm 1$  nm. The corresponding band in the phosphorescence portion of the spectrum is at  $501 \pm 1$  nm. With regards to the solvent effect on the absorption spectra of **1** at room temperature, we observed small red

shifts accompanied by the loss of some spectral structure going from non-polar to polar media, which we attributed to the effect of polarity on both the  $n,\pi^*$  and  $\pi,\pi^*$  transitions. The observed fluorescence spectra exhibit an approximate mirror image reflection of the lowest transition band of their respective solvent dependant absorption spectra [6], Figure 2.

This behavior is typical of excited states that are very similar in nature to the initial ground state, *i.e.* **1** does not exhibit an increase in basicity resulting in protonation of the photo excited molecule. Additionally, the possibility that either moisture or alcohol was complexed to crystalline **1**, thus altering the behavior of the non-polar solvent system, is precluded by the absence of oxygen in an elemental analysis of the material. Therefore, the lack of any solvent affect at 77 K coupled with the fact that the fluorescence emission is analogous to that exhibited by the hydrocarbon parent can only be due to a  $\pi,\pi^*$  state being responsible for the emission.

In continuing the luminescence spectroscopic work at 30.0 °C, no phosphorescence is observed in any of the spectra. The behavior of the fluorescence emission, though, now resembled the low temperature behavior of other monoazaaromatic compounds. The emission spectrum of **1** in cyclohexane shows numerous bands, with the 0-0 band located at 365.8 nm. In going to acetonitrile, the spectrum was red-shifted and no longer exhibited numerous bands. In this instance, the spectrum exhibited two maxima separated by only a very shallow minimum. Finally, in going to the three 2-propanol solutions, neat, 9:1 2-propanol/water and 4:1 2-propanol/water, the spectrum exhibited a skewed gaussian shape with 0-0 bands at 376.0, 378.5 and 380.3 nm, respectively, Figure 3. Accompanying this red-shift in the fluorescence spectrum was a  $\Phi_f$  better than fiftyfold larger than that observed with non-polar conditions [7-14].

The red-shift and fluorescence enhancement noted above is due entirely to polarity and not hydrogen-bonding of **1**. This fact is clearly illustrated by the effect of adding small amounts of concentrated strong acid to 9:1 aqueous 2-propanol. The addition of either 37% hydrochloric acid (HCl) or 98% sulfuric acid (H<sub>2</sub>SO<sub>4</sub>) resulted in fluorescence quenching accompanied by the appearance of very weak, broad and featureless emissions in the tail of the fluorescence spectrum. It appears that this is a protonated excimer of **1** based upon the magnitude of the spectral shift and the lack of any change in the absorption spectrum.

Additional evidence for the quenching effect of hydroxyl groups on **1** is observed in the determination of the absolute fluorescence quantum yield. Using 9,10-diphenylanthracene (DPA) as the actinometer, with a known  $\Phi_f = 0.93 \pm 0.03$  which is essentially independent of solvent [15],  $\Phi_f$ s were calculated for neat 2-propanol, 4:1 (v/v) 2-propanol/water and 9:1 (v/v) 2-propanol/water

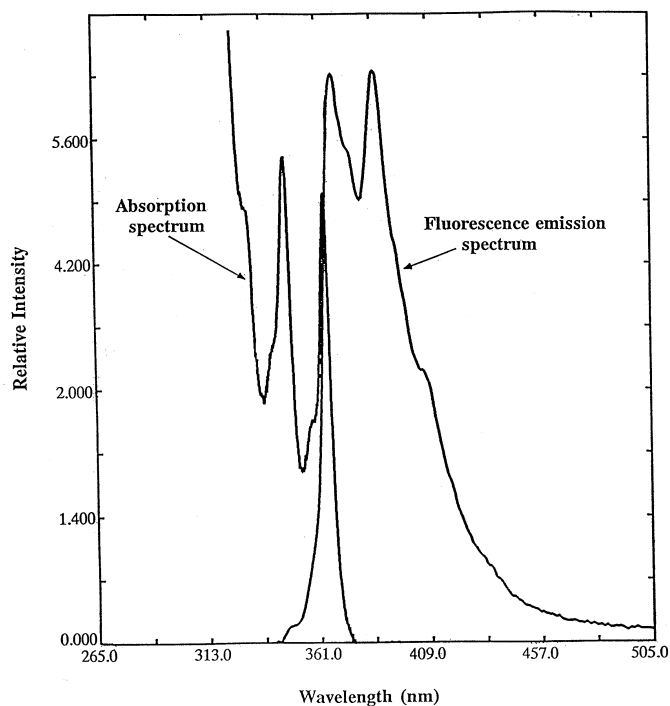


Figure 2. Comparison of the fluorescence emission spectrum of 6-phenanthridinecarbonitrile with its lowest absorption transition band in 9:1 2-propanol/water at 30 °C.

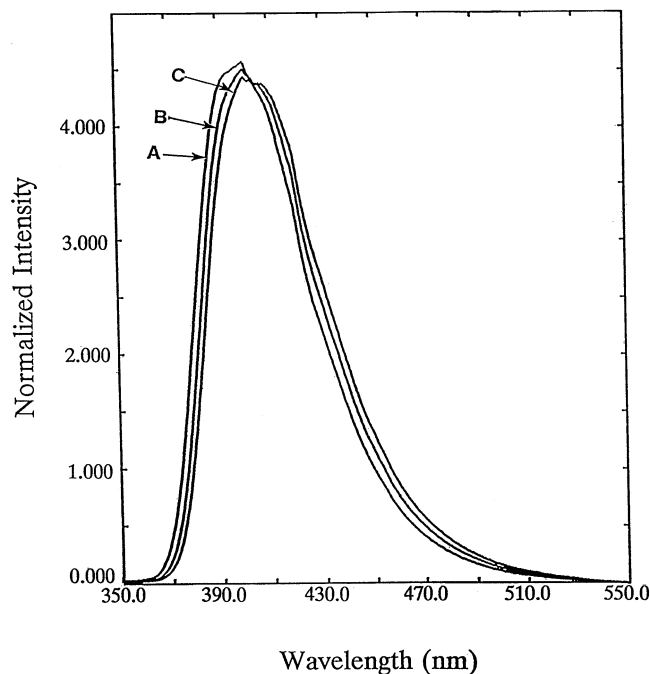


Figure 3. Fluorescence spectra of 6-phenanthridinecarbonitrile in the solutions: A, 2-propanol; B, 9:1 2-propanol/water; C, 4:1 2-propanol/water. The spectrum was corrected for non-linear instrument response.

using dilute solutions which had absorbances of  $0.035 \pm 0.005$  at the selected excitation wavelength for a 1.000 cm cuvette. The  $\Phi_f$ s were calculated using equation (1) [15,16] [Table 1], where 6-PhCN represents the appropri-

$$\Phi_{6-PhCN} = \Phi_{DPA} \times \frac{\text{Area}_{6-PhCN}}{\text{Area}_{DPA}} \times \frac{\text{Abs}_{DPA}}{\text{Abs}_{6-PhCN}} \times \frac{(n_{D6-PhCN})^2}{(n_{DDPA})^2} \quad (1)$$

Table 1

The Effect of Solvent Polarity on the Position of the Fluorescence A, Band and the Magnitude of  $\Phi_f$  for 6-Phenanthridinecarbonitrile

Solvent	$\lambda_{0,0}$ (nm)	$\Phi_f$
Cyclohexane	365.8	----
2-Propanol	376.0	$0.227 \pm 0.003$
9:1 2-Prop/H <sub>2</sub> O	378.5	$0.240 \pm 0.002$
4:1 2-Prop/H <sub>2</sub> O	380.3	$0.253 \pm 0.004$

ate aqueous 2-propanol solution for **1**, Area represents the spectral integration corrected for non-linear instrument response, Abs represents the absorbance at the excitation wavelength of 341.0 nm and  $n_D$  represents the index of refraction of the medium at a given temperature, which in this case was 30.0 °C. All information was determined using argon deaerated solutions.

The  $\Phi_f$  for the three solutions were  $0.227 \pm 0.003$ ,  $0.240 \pm 0.002$  and  $0.253 \pm 0.004$ , respectively. The increase of the mole fraction of water present is accompanied by a 5.7% and 11.1% increase in  $\Phi_f$ . At the same time as the

fraction of water increased, the  $pK_a$  of the aqueous 2-propanol solution was reduced. Therefore, unlike many other monoazaaromatic compounds, **1** is quenched by hydrogen-bonding interactions, though this situation is not unique as Hurtubise *et. al* have shown that water quenches the fluorescence of several benzoquinolines absorbed onto solid surfaces more effectively than does oxygen [17-21].

In the absence of flash photolysis measurements to determine the effect of water on the excited state lifetime ( $\tau$ ), oxygen quenching was determined for **1** in aqueous 2-propanol solutions, Figure 4. Ware has shown that oxygen quenching is strictly diffusion controlled over a wide

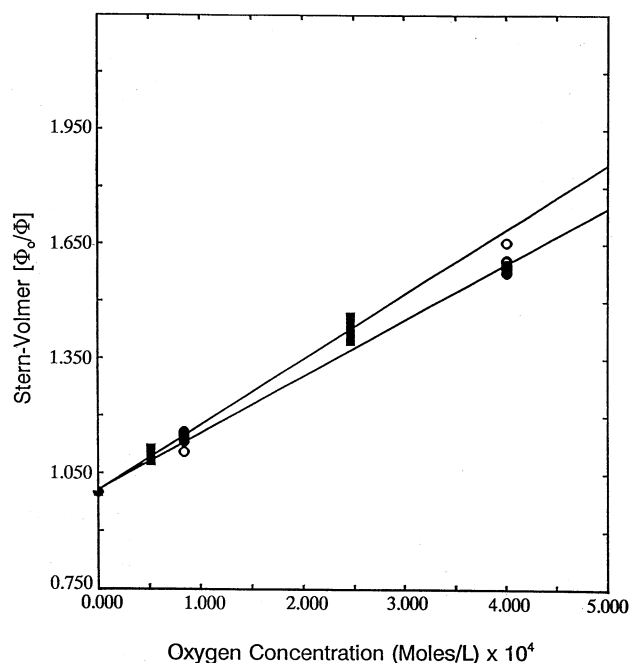


Figure 4. Stern-Volmer oxygen quenching plot for 2-phenanthridinecarbonitrile in aqueous 2-propanol: 9:1 2-propanol/water (○); 4:1-2-propanol/water (■).

range of solvents and viscosities [22]. Determination of Stern-Volmer constants for the three solvent conditions provided the means of determining the value of  $\tau$ , as the slope =  $k_{\text{quench}} \tau$ . Since oxygen is diffusion controlled,  $k_{\text{quench}} \tau = k_{\text{diff}}$ , and Ware has shown that for a small molecule such as oxygen, the following form of the Debye equation is the appropriate form for estimating the diffusion rate constant:

$$k_{\text{quench}} = k_{\text{diff}} = \frac{8RT}{300\eta} \quad (2)$$

where R represents the gas constant ( $8.31 \times 10^7$  erg mol<sup>-1</sup> K<sup>-1</sup>), T represents the temperature in K and  $\eta$  represents the diffusion coefficient in g sec<sup>-1</sup> cm<sup>-1</sup>. Using equations 2, one

obtains values for  $\tau = 3.4, 56$  and  $88$  ns, beginning with neat 2-propanol. There are limitations on the accuracy of this calculation, but the predicted trend should be correct. The net effect of the introduction of water as part of the solvent system results in an increase in the lifetime of the excited state.

Finally, we still do not have a satisfactory explanation for the effect of *cis/trans*-piperylene on the fluorescence of **1**. Under the conditions used for the reaction with the diene, the singlet state of **1** would have a 0-0 band corresponding to an energy of  $75.5 \text{ kcal mol}^{-1}$ . Since the singlet state of the diene is at  $88 \text{ kcal mol}^{-1}$ , it seems highly unlikely that quenching of the singlet state of **1** would occur. Based on the phosphorescence emission at  $77 \text{ K}$  the 0-0 band corresponds to a triplet energy of  $57 \text{ kcal mol}^{-1}$ . This state could be quenched by piperylene with a triplet energy of  $58.5 \text{ kcal mol}^{-1}$ , but this mechanism would require some sort of rapid equilibrium between singlet and triplet excited states [23,24].

### Conclusions.

Based on the evidence previously discussed, the most reasonable explanation for the photochemical behavior of **1** in aqueous 2-propanol involves the  $\pi, \pi^*$  excited singlet state in a hydrogen atom abstraction process. This process is known to have low quantum mechanical probability, though it is still a viable process. Additionally, the lack of a two electron voltaic reduction of **1** would indicate that decyanation does not occur in a manner consistent with previously studied pyridinecarbonitriles.

The presence of an ESR signal at ambient temperatures accompanied by the *cis/trans*-piperylene quenching of the fluorescence of **1** both indicate a singlet state as the principal reactive excited state. The solvent effect on the fluorescence spectrum is consistent with a lowest excited singlet state which is  $\pi, \pi^*$ . The very low reactivity of this molecule indicates that the major pathways involved in the photochemical behavior of **1** under these conditions are fluorescence decay to the ground state and internal conversion from the lowest excited singlet state to the ground state.

The mechanism for the photochemical coupling reactions of **1** can then be explained by a sequence which includes: absorption of a photon of light followed by internal conversion to the lowest excited singlet  $\pi, \pi^*$  state, hydrogen atom abstraction by the nitrogen in the ring and reversible coupling between the 6-position on the ring to either another 6-cyanophenanthridinyl radical or to a dimethyl ketyl radical generated by the hydrogen atom abstraction from isopropyl alcohol. The appropriate coupling product is then formed by elimination of the proper number of hydrogen cyanide molecules.

The only reaction that probably involves a triplet state is the benzophenone photoreaction with **1**. The fact that very little benzopinacol is formed after a prolonged irradiation time is clearly indicative of triplet energy transfer to **1**.

Therefore, it is likely that hydrogen atom abstraction occurs from an  $n, \pi^*$  triplet state of the benzophenone sensitized **1** molecule, in accordance with El-Sayed's Rule, followed by coupling to a diphenyl ketyl radical.

However, since **1** has absorption bands in the same region, products may also be formed by the mechanism described above involving the  $\pi, \pi^*$  lowest excited singlet state of **1** formed by reverse intersystem crossing.

## EXPERIMENTAL

### Routine Laboratory Procedures.

Routine proton NMR were recorded on a Varian EM 360-A or a EM 390 NMR spectrometer. The carbon-13 spectra were run on a Varian CFT 20 NMR. All chemical shifts are reported in parts per million (ppm) relative to the shift observed for tetramethylsilane. Deuterated solvents were obtained from Aldrich Chemical Company. Infrared spectra were recorded on a Beckman Acculab IV or a Perkin Elmer Model 381 Infrared spectrophotometer. Polystyrene was used for the calibration of both portions of the spectral recording range. Liquid sample were run neat on either sodium chloride or potassium bromide windows and solids were run as pellets made with spectrograde potassium bromide. Ultraviolet-visible absorption spectra were run on a Cary 15 or 210 Model Recording Spectrophotometer, a Beckman DU series Spectrophotometer or a Perkin Elmer Lambda-5 UV-Visible Spectrophotometer [25] interfaced to a Dell 12 MHz 80286/80287 computer to allow acquisition of digitized spectra. Melting points were determined on either a Thomas-Hoover or Mel-Temp capillary melting point apparatus and are uncorrected. High performance liquid chromatography (HPLC) was carried out on an IBM 3345 Tertiary Gradient HPLC equipped with an analytical column (octadecyl stationary phase,  $4.5 \times 250 \text{ mm}$ ) and a  $254 \text{ nm}$  wavelength detector (absorbance) using 5:1 (V/V) acetonitrile/water as the eluent.

All of the ESR spectroscopy work was carried out using a Bruker ER 220 D-LR Electron Paramagnetic Resonance Spectrometer [26] interfaced to a 16 kilobyte microcomputer. The instrument was equipped with an ER 4102 ST Universal X-band resonator having a rectangular cavity resonance in the TE-102 mode, that operates with a nominal center frequency of 9.6 gigahertz and is fitted with a grid for horizontal irradiation of the sample. Irradiations for ESR studies were carried out using an Oriol Instruments [27] 1000 watt high pressure mercury vapor lamp. The unit uses a water jacket located between the focusing lens and the mercury lamp to filter out all high energy ultraviolet light below  $190 \text{ nm}$ . The initial uncorrected total luminescence spectra of **1** at low temperature and relatively high concentration were recorded on a Farrand Spectrofluorimeter MK-2 [28] equipped with a 150 watt Xenon arc lamp. Spectra were recorded with the excitation wavelength monochromator set at  $205, 255,$  and  $320 \text{ nm}$ , respectively for the emission wavelength range of  $300$  to  $600 \text{ nm}$ . The spectra were recorded with the emission wavelength monochromator set at a scan speed of  $100 \text{ nm}$  per minute with the excitation slit set at  $2.5 \text{ nm}$  and the emission slit set at  $1.5 \text{ nm}$ .

The remaining low temperature luminescence work was carried out on a Hitachi/Perkin-Elmer MPF-2A Spectrophoto-

fluorimeter [25] equipped with an Osram 150 watt high pressure Xenon arc lamp and a Hamamatsu R106UH ultra-high gain photomultiplier tube. All spectra recorded on this instrument were done in ratio mode. The low temperature work in liquid nitrogen involved replacing the instrument's standard output to a QPD-33 strip chart recorder with an in-house designed amplifier. This unit served to interface the instrument to a CompuPro CPU-286/287 8 MHz microcomputer that digitized spectral intensities at 1.0 nm increments with a 50 KHz 1/0 Technology A/D/A board at a scan speed of 200 nm per minute. Spectra were recorded with the excitation wavelength monochromator set at 320 nm for the emission wavelength range of 330 to 600 nm. The excitation wavelength monochromator slit was set at 1.5 nm and the emission slit set at 2.5 nm. Spectra were recorded at 77 K, using a 1.5 mm I.D. quartz cell immersed in a vacuum-jacketed quartz dewar filled with liquid nitrogen.

Prior to measurement of the quantum yield of **1** and oxygen quenching effects at 30.0 °C, the MPF-2A fluorimeter was upgraded. This involved replacement of all the instrument's electronics to permit interfacing to a Dell Corporation 12 MHz 80286/80287 IBM AT clone computer equipped with a 12-bit Data Translation 27.5 MHz DT2801-A A/D/A board. The two monochromators were set to band pass openings of 3.0 nm, and intensities were recorded at 0.25 nm increments. Temperature control was maintained by a Neslab RTE-4DD thermostatic bath and was monitored with an Omega 199P1 Digital Thermometer. The entire time required to execute a typical emission scan, including test of baseline drift, ranged from 3.2 to 4.1 minutes.

The instrument response correction factors for non-linearity of the MPF-2A were determined by following the procedure outlined by Parker [29]. This procedure generates emission spectra corrected so that the relative integrations were proportional to the quanta emitted per unit time. An Eppley Laboratory tungsten ribbon filament lamp (G.E. 30A/T24/17) calibrated to a National Bureau of Standards primary black body source was operated at 30 amperes. The light radiated from this lamp was reflected off a pressed pellet of barium sulfate into the emission monochromator. The pellet was placed in the fluorimeter's solid sample pellet mount, and the tungsten lamp's output was reflected off the barium sulfate pellet at a 90° angle. The energy emission spectrum was then recorded from 220 to 800 nm for several band pass sizes in the range of 1.0 to 10.0 nm. The limited number of points in the calibrated output curve for the standard lamp necessitated using polynomial fitting to generate accurate correction factor curves. The range of 220 to 290 nm was fitted with a 4<sup>th</sup> degree polynomial, 290 to 450 nm with a 5<sup>th</sup> degree polynomial, and 450 to 800 nm with another 5<sup>th</sup> degree polynomial [30]. The instrument response correction factors for the fluorimeter were then calculated by dividing the known lamp energy by the observed lamp energy after having been corrected for the reflectance of barium sulfate [31]. Results are given with respect to wavelength.

Irradiation of 6-Phenanthridinecarbonitrile at 2537 Å in Neutral Aqueous 2-Propanol with *cis/trans*-Piperylene.

A solution of **1** (1.03 mmoles) and a molar excess of *cis/trans*-piperylene in 150 mL of 9:1 (v/v) 2-propanol/water was deaerated

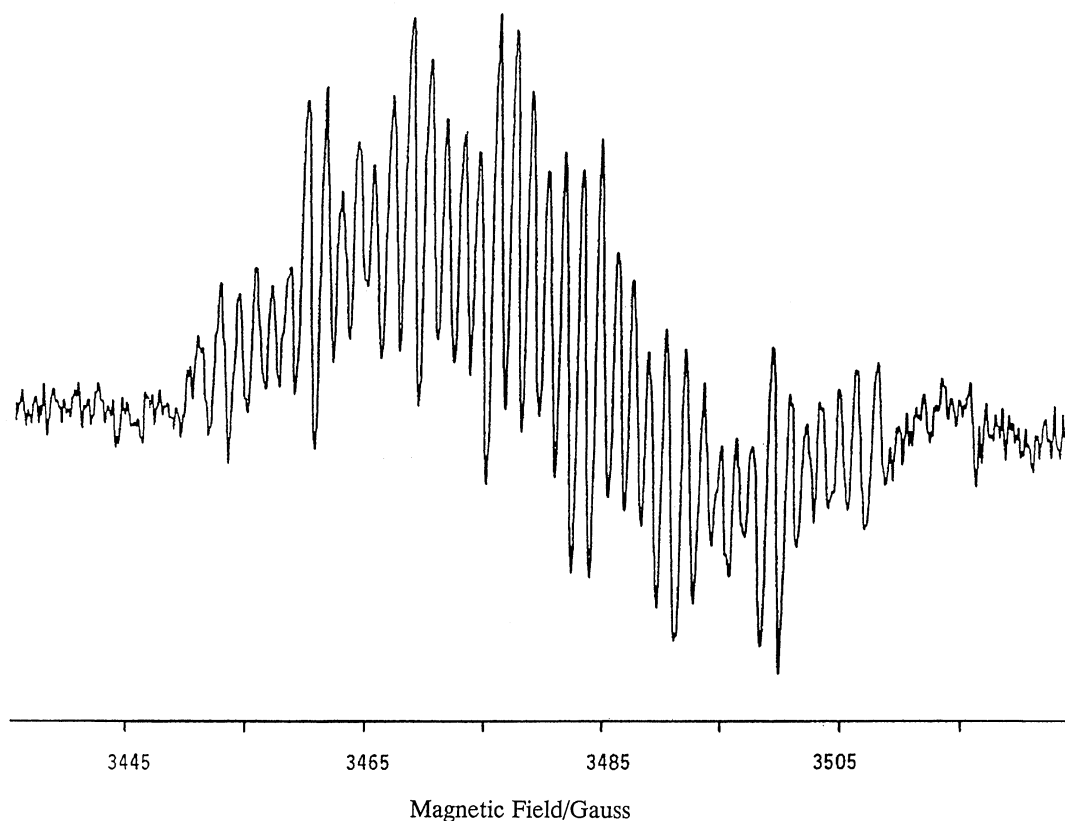


Figure 5. ESR spectrum of 6-cyanophenanthridinyl radical in absolute alcohol at ambient temperature.

with argon bubbling and irradiated for 16 hours at 2537 Å in a Rayonet reactor. During this time the solution changed from colorless to deep orange. Upon analysis by TLC, very little reaction was found to have occurred, indicating that the reaction was quenched by the diene.

#### Electron Spin Resonance Studies of 6-Phenanthridinecarbonitrile in Anhydrous Ethanol.

The irradiation of an oxygen free solution of **1** in absolute ethanol was done with a 1000 watt high pressure mercury arc lamp focused on the cavity of the ESR spectrometer. Low temperature work was done in pyrex at temperatures between -180 °C and -130 °C using deoxygenated solutions of ethanol in a solid matrix. Work done at ambient temperatures utilized a quartz flat cell where the sample and flow cell system had been deoxygenated with argon prior to recording spectra.

In the ESR spectroscopic measurements of **1**, only a single Lorentzian shaped peak was observed at low temperatures. Further, the rate at which the steady-state equilibrium of the signal intensity occurred exceeded the time scale of the ESR spectrometer. A similar behavior was noted in the decay of the signal upon termination of sample irradiation. Due to these factors as well as the observations at ambient temperatures, no further spectroscopic work was done at low temperatures.

The observed ambient temperatures ESR spectrum of **1** was highly complex and not a typical radical spectrum. Instead it exhibited what is commonly known as an envelope shape [32], Figure 5. Unfortunately, the poor signal to noise ratio precluded any attempts to measure the hyperfine coupling constants. The effect of the addition of a small amount of concentrated hydrochloric acid was consistent with the result reported above. The signal intensity dropped off dramatically for the protonated molecule.

Despite the problems with the spectral resolution, the free spin value,  $g_e$ , was determined at both low and ambient temperatures. A value of 2.0043 was observed at 125 K and values of 2.02539 and 2.04781 were obtained for different portions of the spectrum at ambient temperature. The low temperature value is very close to the 2.00232 theoretical value of a free electron, hence there is little spin orbital coupling effect [33]. Due to the disparity in the  $g_e$  values measured for two different portions of the ESR spectrum at room temperature, the correct value, and therefore, the magnitude of the spin orbital coupling effect could not be determined [34].

In addition to measurement of the complete ESR spectrum of **1**, kinetic measurements were made to determine the rate of formation of the ESR signal as a function of light intensity. Several neutral density filters were placed directly in front of the cavity opening to regulate the light intensity. A plot of the logarithm of the initial rate of radical formation,  $v_0$  ( $\text{mol s}^{-1}$ ), versus the logarithm of the relative light intensity,  $I$  ( $\text{photons s}^{-1} \text{cm}^{-2}$ ), gave straight line with a slope of  $1.06 \pm 0.05$  ( $\text{mol photon}^{-1} \text{cm}^{-2}$ ). This corresponds to a monophotonic process for the formation of the radical (Figure 1).

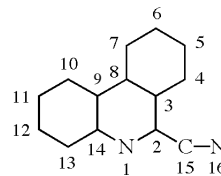
The above results for **1** are not inconsistent with an excited singlet state as the primary pathway for both reaction and deactivation, although the possibility of some triplet formation is not completely eliminated.

#### Molecular Orbital Electron Spin Density Calculation of 6-Phenanthridinecarbonitrile.

Due to the inability to calculate electron spin densities from the ESR spectral coupling constants for **1**, a theoretical calculation was

made to provide some insight into the expected distribution pattern of spin densities. The procedure for calculation of the self-consistent field of the electron spin distribution in  $\pi$ -electron radicals presented by McLachlan was used for this determination [35]. The results from this calculation are presented in Table 2. While these calculations may not be exact, if one assumes that the trend is reasonable, from the data in Table 2, the two ring positions most likely to have the greatest  $\pi$  electron density are positions 1 and 2.

Table 2  
Hückel Molecular Orbital Calculations of the  $\pi$  Electron Densities for 6-Cyanophenanthridinyl Radical



Location	$\pi$ electron density	Location	$\pi$ electron density
1	0.23066704E + 00	9	0.47237920E-01
2	0.12728275E + 00	10	-0.54431331E-02
3	-0.20668587E-01	11	0.10719527E + 00
4	0.88831541E-01	12	-0.38270019E-01
5	-0.13822789E-01	13	0.11719340E + 00
6	0.47646563E-01	14	-0.83889507E-02
7	0.34182274E-01	15	-0.26091223E-01
8	-0.13388299E-02	16	0.31214825E + 00

#### Cyclic Voltametry Measurement of 6-Phenanthridinecarbonitrile.

The electrochemical behavior of **1** was studied in dimethylsulfoxide by cyclic voltametry against a standard calomel electrode (SCE). The cyclic voltamogram gave a single pair of reversible peaks, clearly indicating that **1** does not form a dianion. Though dianion formation is important in the decyanation of some cyanopyridines [36,37].

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