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PROGRESS REPORT

STABILITIES OF NITROGEN CONTAINING HETEROCYCLIC RADICALS AND GEOMETRICAL INFLUENCES ON NON-RADIATIVE PROCESSES IN ORGANIC MOLECULES

NASA-CR-136620) STABILITIES OF NITROGEN CONTAINING HETEROCYCLIC RADICALS AND GEOMETRICAL INFLUENCES ON NON-RADIATIVE PROCESSES IN ORGANIC MOLECULES (California Univ.) 82 p HC $6.25 CSCL 07C N74-15807
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by

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INTRODUCTION

The first report submitted (July 1969) under the title of this grant dealt with the theoretical aspects of the "Geometrical Influences on Non-Radiative Processes in Organic Molecules" together with some experimental investigation into this problem in the case of aryldiazonium salts. The second report, covering the period from July 1969-July 1970 dealt almost entirely with the "Stabilities of Nitrogen Containing Heterocyclic Radicals". Both the theoretical and experimental aspects of this problem were dealt with

The following report will deal with the termination of the radical study and a return to the problem of "Geometrical Influences on Non-radiative Processes in Organic Molecules". This report will be split into three main sections. Section A, is entitled "Radical Studies". Section B, entitled "Studies in Radiative and Non-radiative Processes in Heterocyclic Molecules". Section C is entitled "Photophysical and Photochemical Processes in Aryldiazonium Salts".

Work in sections A and C was carried out with the aid of Dr. Buddy Chang. Work in section B was carried out with the aid of Dr. Paul Horowitz and Dr. Dan Lerner.

A. RADICAL STUDIES

1. Object of this work The simple radicals generated from the removal of a hydrogen atom from a nitrogen atom in the molecules pyrrole (I), imidazole (II), indole, and carbazole have not been detected by electron spin resonance measurements. However,

I

II

III

the polyphenyl derivatives of the radicals of pyrrole and imidazole have been detected by ESR measurements.[1,2] The practical interest in the radical from II results from the importance of imidazole in biochemical processes.[3,4] Theoretically, we have shown that the electronic structure of the imidazyl radical is anomalous.[3] In the case of the radical from I, the theoretical calculations clearly show that the structure is that of a pi-radical, i.e., the odd electron "spends" its time in a pi-orbital. It is theoretically more accurate to state the irreducible representation of the electronic wave function of the radical of pyrrole (pyrryl) is antisymmetric to the symmetry operation of reflection through the plane of the molecule. In contrast, the imidazyl radical is calculated to be symmetric to this same operation and is classified as a sigma radical. This is strange because the simple radical NH_2 is pi and corresponds to pyrryl and not imidazyl. The antisymmetric electronically excited state of NH_2 is only within about 1 ev of the ground state,[5] i.e., both the symmetric and antisymmetric excited states are very nearly degenerate.

In addition to these above considerations the radicals from compounds I and II are related to what can be termed as the "mother" compound III, the cyclopentadienyl radical. Pyrryl and imidazyl are aza and diazacyclopentadienyl radicals respectively. Again the electronic structures of these radicals would be of interest considering that the corresponding electronic degeneracy in III would be lifted on aza-substitution.[6]

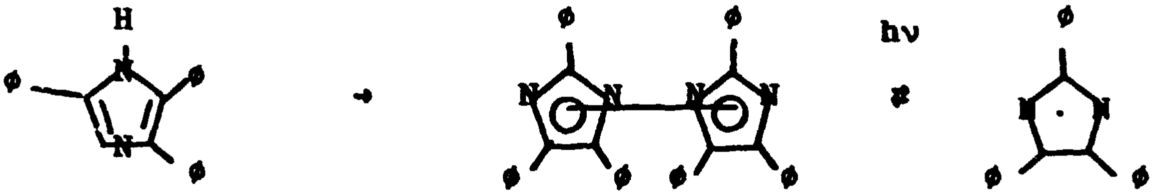
Thus considerable effort was expended,[3] without success, in attempts to generate the radicals of a number of related heterocyclics. In the previous years' reports[3] we detailed a number of these attempts. Here we will terminate the work towards this goal with a final discussion of the problem.

2. Attempts at Photolytic Generation

a) Cyclopentadienyl Radical It was found, in agreement with the literature work,[6a] that the photolysis of a frozen mixture of di-t-butyl peroxide and cyclopentadiene at -120C yielded (Figure 1) a 6 line ESR spectrum with the intensity ratios of 1/4/9/9/4/1. Theoretical for cyclopentadienyl radical is 1/5/10/10/5/1 and it is therefore concluded that the spectrum observed is that of cyclopentadienyl radical.

Identical attempts to generate radicals by the photolysis of frozen mixtures containing pyrrole, carbazole, imidazole, benzimidazole, and carbonyldiimidazole yielded <u>no</u> detectable radicals. In the particular case of pyrrole discoloration of the photolyzed mixture was noted.

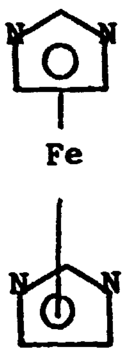
b) <u>2,4,5-triphenyl imidazyl Radical</u> 2,4,5-triphenyl imidazole is commercially available under the name of Lophine-X. This material was oxidized with potassium ferricyanide in ethanol-potassium hydroxide to yield the dimer material (IV).[7]



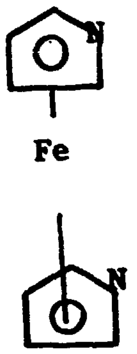
IV

We were able to obtain the radical of this material, as described in the literature, by direct photolysis of the dimer in solution. The ESR spectrum of this material is shown in Figure 2. The recent literature shows that ENDOR measurements are available on this radical.[8] The radical is clearly a pi-radical from both the ESR and ENDOR measurements.

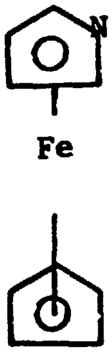
c) <u>Thermolysis Methods</u> It is experimentally known that cyclopentadienyl radical (III) can be trapped at -196 by thermally decomposing ferrocene (dicylopentadieyl iron) in a gas stream.[9] Unfortunately neither the imidazole or pyrrole analogs of ferrocene are known (V and VI, respectively). However, the half-analog VII is reported in the literature.[10] We attempted the literature synthesis of this material (VII) and were not successful.



V



VI



VII

In principle, this approach still looks promising since the analog VII is known in the literature. It is also curious as to why the compounds V and VI are not known in the literature. The anions of both pyrrole and imidazole are well known but apparently the reaction of these materials with iron chloride, which is analogous to the classic synthesis of ferrocene from iron chloride and cyclopentiednyl anion, is not known. The pK_a's for proton removal from both pyrrole and imidazole are lower than cyclopentadiene[11] and it might be guessed that it would be more difficult to form a stable product in which the anions of the two former materials yield a stable product with iron. Still, even if the products were unstable this in itself might provide a convenient route to generation of heterocyclic radicals.

d) Conclusions of this work We have not been able to generate the simple heterocyclic radicals pyrryl, imidazyl, nor the corresponding radicals from indole, benzimidazole, and carbazol. We decided after about 16 months of work in this area to cease attempts at such generation and go to work which would produce immediate results. Still, the generation of these types of radicals are of theoretical and practical interests, especially in the cases where there is possible revalence to biological problems. In the case of the simpler radicals, pyrryl-imidazyl, the polyphenyl derivatives are known and easily generated. Because of the dispersal of spin density and steric factors, these radicals should be much less likely to couple in solution. On the other hand, the smaller basic radicals pyrryl and imidazyl would probably couple at high rates yielding the typical detection problem analogous to simple hydrocarbon radicals. Under such restrictions the radicals could only be detected under steady state conditions using flow systems or at low temperatures under state photolytic generations. In addition, there is no assurance that in pyrrole, for instance, the N-H bond is weaker then the C-H bond. Oxidation, electrolytically, of the anions of these various species is, in principle, possible. We did not succeed however in aqueous solutions. Direct preparation of the water free anion salts followed by flow chemical oxidation would appear to be a convenient route. Finally the above-mentioned preparation of the iron salts is worth detailed investigation. Thus, in spite of our own failures, it indeed appears that the area remains open for other investigators.

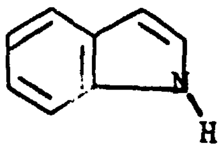
SECTION B RADIATIVE AND NON-RADIATIVE PROCESSES IN HETEROCYCLIC MOLECULES

1. The Theoretical Problem One of the central problems in the area of "Geometrical Influences on Non-Radiative Processes in Organic Molecules" has to do with what is called the "energy gap law".[12] Kasha's Rule states,[13] essentially that emission of light always occurs from the lowest excited state of a particular multiplet. Thus in normal organic molecules, which have even numbers of electrons and therefore have filled shell ground states this means that fluorescence always occurs from the lowest excited singlet. Another type of emission, longer lived, phosphorescence, always occurs from the lowest triplet state. Exceptions to Kasha's rule were discovered by Kasha himself,[14] namely in the case of the azulenes. In azulene the energy gap between the lowest excited singlet, S_1, and second excited singlet, S_2, is about 14,000 cm^{-1}, which is nearly the same value as the S_1-S_0 energy gap.[15] In the case of azulene fluorescence is only readily detected from the S_2 to the S_0 (ground) state.[16] It is now known that a very weak emission, detectable by photon counting techniques, occurs from S_1 to S_0 and from S_2 to S_1.[16] The theoretical rationalization for emission from the S_2 state is found in what is generally called the energy gap law which essentially states that radiationless processes between 2 electronic states are dependent on the energy separation between them.[17] That this actually occurs is obvious from the fact that fluorescence occurs at all since this radiative process must compete with the radiationless process between the same 2 states, as well as into the triplet manifold. In

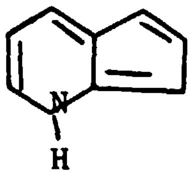
this latter process, the energies of the excited singlet state, S_1, and some triplet state T_n may in fact be very close but the rate of the process is dominated by the degree of forbiddeness of the change in electron multiplicity.

The strangest thing about the azulene anomalous emission is that there are very few examples of which yield identical behavior.[18] Recently, most of the examples of anomalous emission come from materials having very close lying S_2-S_1 states, so close in fact that there are very few vibrational states which allow for coupling between the electronic states.[19] Under such conditions anomalous emission is promoted by a small energy gap.[19,20] However, large gap or moderately largegap materials are rare in the literature. The reason for this is largely due to the fact that most of the materials subject to detail physical chemical investigation are hydrocarbons, usually alternates. Azulene type molecules have been investigated for emission properties. One set of authors failed, however, to present fluorescence excitation curves of the materials they dealt with and thus the emission they observed is not necessarily the emission of the structures they described.[21] This is a classical problem in emission spectroscopy; anomalous emission is most likely attributable to impurities unless proven otherwise. In alternate hydrocarbons, large energy gaps are unlikely,[22] this resulting from purely theoretical reasons partly explainable by invoking the pairing rule.[22,23] Thus any search for candidates having large energy gaps immediately should rule out the alternate hydrocarbons. Many non-alternate hydrocarbons have large energy gaps, but with the exception of azulene have low thermal stabilities. Some, as already mentioned have been studied. The only other class of materials which might be investigated lie in the heterocyclics. This is our approach.

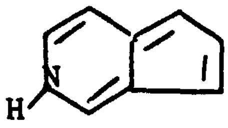
The initial search for candidates of materials having unusual photophysical properties was done by examining the literature. In particular, one class of molecules has experimental spectra[23] which indicate a large separation in energy between the first (S_1) and second (S_2) excited singlet states. The first class of materials are isomers of indole (VIII). Indole, itself, has a fairly narrow S_2-S_1 gap, and is theoretically related to naphthalene.[24] Previous work has commented on the spectral relationship of 1- and 2-pyrindene (IX and X) with azulene.[25] These materials are isomers of indole but are also thermally unstable, existing only when frozen into the shown tautomeric form when H = alkyl. No



VIII

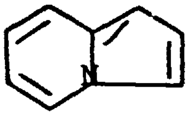


IX



X

photophysical studies are reported on derivatives of IX or X, with the exception of the 1-aza-derivative of IX.[26] A third molecule, indolizine (XI) is fairly stable and has a S_2-S_1 energy gap of around 8000 cm^{-1}, not quite that of azulene (14,000 cm^{-1}). Thus studies were initiated on indolizine and some aza-indolizines.



XI

2. Theoretical Calculation of the Singlet and Triplet Manifold Energies of Indolizine and Some Related Aza-Derivatives

The literature reports[23] the singlet-singlet absorption spectra of a number of indolizines. Qualitative reports of the emission (fluorescence) of these materials abound in the synthetic literature.[27] No quantitative emission studies are reported. First, we report here some pi-electron calculations of the spectral features of these materials. Some previous work has been presented in the literature of the singlet manifold.[28] However, the reported calculations were not calibrated for the positions of the 0-0 vibrational transition of each electronic transition but for the center of the Franck-Condon maxima. Since the type of calculations we will present here are semi-empirical, there is always some doubt as to the quantitative reliability of such calculations in any case. The best that can be anticipated is, perhaps, an accuracy of within 0.2 electron volts (ev) for the first and second triplet states. This is only if the calculation is standardized for some representative structures.

Method of the Calculations The "best" approach to pi-electron calculations of electronic spectra is the classic one of Pariser, Parr, and Pople.[28] This involves the calculation of the ground state wavefunction using the self-consistent molecular orbitals obtained from the Hartree-Fock operators. After obtaining a series of one electron molecular orbitals for the ground state a series of virtual excited states are generated from the same orbitals and "mixed" using the electron repulsion operator. This method is well discussed in a number of texts and no further discussion will be made here.

The method is semiempirical and requires the use of certain experimentally determined parameters. In the calculations presented here the parameters used are listed in Tables 1 and 2. The critical parameters in electronic transition calculations are the resonance integrals listed in Table 2. The other parameters listed in Table 1 have some influence on these quantities, especially the one centered electron-electron repulsion integrals. In addition the method of calculation of the two centered electron repulsion integrals has some influence on the singlet-triplet splitting, i.e., the relative energies of the triplet and singlet manifolds. The absolute value of energies of the electronic transitions, however, is strongly influenced by the resonance parameters listed in Table 2. The values listed in Table 2 were selected from sample calculations on indole (VIII), 1-pyrindine (IX), 1-aza-1-pyrindine (XII), purine (XIII), and adenine (XIII). Since it is known that the Mataga method[29] for the calculation of the triplet state energies gives too low values, the normal Pariser-Parr method was used here for the computation of the 2-centered electron-electron repulsion integrals.

A comparison of the computed positions of the first and second singlet-singlet transitions in compounds VIII, XII, XIII, and XIV is shown in Table 3. In addition is shown the value of the lowest triplet. Experimentally,[30] in both purine (XII) and adenine (XIV) the two observed transitions lie in the same energy region and separate evaluations of their energies and intensities have not been possible. This has been often noted in the literature.[30] In the case of the triplets energies the calculated values seem consistently too low by several tenths of an electron volt. This is not unusual in pi-electron calculations of singlet and triplet manifolds.

We have pointed out in the literature[28] the reason why a molecule like XI has a much lower transition energy than the indole or polyazaindole structures, like adenine or the purines. The reasons are complex and related to a perturbation treatment of the spectral transitions in the "mother" compound indenyl anion. However, another almost equivalent rationalization can be given by saying that indole itself is benzenoid and will have benzene-like spectral characteristics, perturbationally related to the transitions in benzene itself at 250 nm and 200 nm, but red shifted. However the other molecules like indolizine itself, or 1- and 2-pyrindine are quinoidal or polyenic in nature, having little benzenoid characteristics and being less aromatic. A molecule having low aromaticity will have a low ground state stability giving rise to a lower splitting between the ground state and lowest excited state; i.e., a lower transition energy compared with resonance stabilized systems. All these above arguments are qualitative rationalizations of what computationally occurs.

Using the parameters selected for obtaining the spectra of the molecules shown in Table 3 we computed the singlet-triplet manifold of indolizine (XI) and 1-aza-indolizine (XV), shown in Table 4. The singlet manifold for indolizine is in good agreement with the observed spectral features in Figure 3. Unfortunately we have not yet been able to experimentally determine the value of the lowest triplet state (T_1). In 1-azaindolizine (XV) the singlet manifold is also in good agreement with experiment. As will be shown later, the lowest triplet state of XV is at 2.85 ev (0-0 transition) which is nearly 0.6 ev higher than calculated, in disagreement with the results obtained in Table 3 where the corresponding difference is nearer to 0.2-0.5 ev. However, we have no other test compounds having non-aromatic structures, like XV, to see if the calculations are reliable. Thus it is conceivable that the calculated triplet manifolds for compounds XI and XV should be moved up by 0.6 ev. The consequence of this will be discussed later. In any case the predicted S_2-S_1 energy gap in XI is about 0.7 ev compared with about 1 ev experimentally. The computed position of the S_1 state lies between the T_2 and T_3 state for indolizine. If all the T states are moved up by 0.6 ev then the S_1 state lies between the T_2 and T_1 state. Without such an adjustment in indolizine, S_1 is nowhere near, energetically, to a triplet state (several tenths of an ev).

A number of related structures are computed and shown in Table 5. Table 5 lists the energies of the S_1 and S_2 states. In addition it lists all computed triplet states lying below the S_1 state. Several things are to be noted. First, a number of compounds having fairly large computed S_2-S_1 energy gaps. These are: IX (1 ev), XIX (1), XX (1), XXII (0.8), XXV (0.8), X (0.8), XXVI (0.8), and XXVIII (1.3). None of these are very near azulene (1.8 ev),[15] although the latter material comes the closest. Most of these materials have not yet been reported in the literature. In addition, the experimental values for compounds XXIV and XXV are approximately 0.5 ev higher than calculated, leaving some doubt as to whether the parameters used are really good for all the materials calculated. However, it is likely that the S_2-S_1 energy gaps are more accurate than the absolute energy values.

As demonstrated in Table V there is one feature of the triplet manifolds of the azaindoles (benzimidazole, as well as the purines) that differentiates them from the non-aromatic materials (the indolizines and the pyrindines). This is the number of pi-triplet states computed to lie between the S_1 state and the lowest triplet T_1. Especially in indole there is a relatively high density of such states, 5 by computation. In purine and adenine (XIII and XIV) there are 3. In the other materials the numbers vary between 2 and 3 (see also Table IV).

Table 1

Coulomb Parameters

Atom	I_p(ev)	Z	$\langle 11\|11\rangle$(ev)
C	11.22	3.25	10.53
N (pyrrole type)	28.16	4.25	15.92
N (aromatic)	14.63	3.90	12.27

I_p = valence state ionization potential, Z = Slater Z value, and $\langle 11|11\rangle$ = one centered repulsion integral.

Table 2

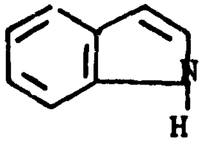
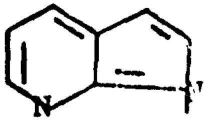
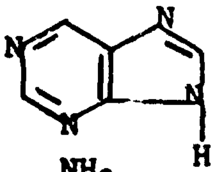
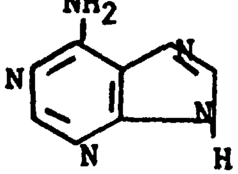
Resonance Parameters

Bond Type	Resonance Integrals (ev)
C-C (formal single)	-2.07
C=C (formal double)	-2.20
C=C (aromatic)	-2.15
C-N (formal single in ring)	-1.84
C=N (formal double)	-2.55
C=N (aromatic	-2.28
C-NH_2 (external amino)	-2.40

Table 3

Calculated and Experimental Pi-Electronic Transitions

Known Materials

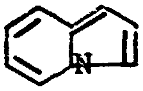
Structure		$S_0 \rightarrow S_1{}^{\pi}$ Calcd.(f)	Obs.	$S_0 \rightarrow S_2{}^{\pi}$ Calcd(f)	Obs.	$S_0 \rightarrow T_1{}^{\pi}$ Calcd.	Obs.	Refs.
	VIII	4.26(0.003)	4.31^a	4.46(0.11)	4.6	2.81	3.06^b	
	XII	2.70(0.04),	2.70^c	3.66(0.15),	3.8	1.75		
	XIII	4.43(0.10)	$4.6^{a,d}$	4.84(0.14)	?	3.35	3.57^e	
	XIV	4.32(0.10)	$4.5^{d,e}$	4.45(0.24)	?	3.02	$3.4\text{-}3.5^e$	

a. This work, acetonitrile.
b. L. Goodman and M. Kasha, J. Mol. Spectr. 2, 58 (1958).
c. Cyclohexane, A. G. Anderson and H. L. Ammon, Tetrahedron 23, 3601 (1967) and Tetrahedron Letters, 2579 (1966).
d. L. B. Clark and I. Terioca, Jr., J. Am. Chem. Soc., 87, 11 (1965).
e. V. Kleinwachter, J. Drabrik, and L. Augenstein, Photochem. Photobiol. 6, 133 (1967).

Table 4

Calculated Singlet and Triplet Manifolds for Indolizine

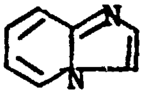
(Electron Volts, oscillator strength)



XI

Exptl.	Calculated	
	——— S_5 (5.58, 0.025)	
	——— S_4 (5.38, 0.623)	
---S_3(5.1)	——— S_3 (5.14, 0.019)	
---S_2(4.19)	——— S_2 (4.16, 0.056)	———T_5 (4.47)
		———T_4 (3.80)
		———T_3(3.69)
---S_1(3.26)	——— S_1 (3.46, 0.060)	
		———T_2 (2.88)
		———T_1 (2.16)
	——— S_0	

Calculated Singlet and Triplet Manifolds for 1-Aza-Indolizine



XV

Exptl.			Exptl.
	S_5 (5.78, 0.283)		
	— S_4 (5.64, 0.273)		
	— S_3 (5.19, 0.282)		
	— S_2 (4.30, 0.010)	— T_5 (4.40)	
		— T_4 (3.98)	
—(3.7)	— S_1 (3.82, 0.063)	— T_3 (3.59)	
		— T_2 (3.31)	---T_1(2.85)
		— T_1 (2.26)	
	— S_0		

Table 5

Comparison of the Computed Number of Triplets States Lying Beneath the S_1 State with Structure

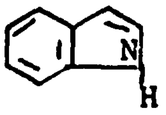
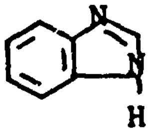
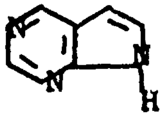
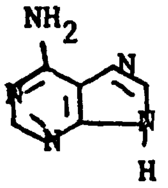
Structure		S_1, (T_1, T_2, etc), S_2 in electron volts	Exptl. $S_1(T_1)$
Azanidoles			
	VIII	4.26, (2.81, 3.54, 3.92, 4.06), 4.46	4.31 (3.06)[a]
	XVI	4.34, (3.30, 3.89, 4.00, 4.13, 4.34), 4.62	
	XIII	4.43, (3.35, 3.83, 4.29), 4.84	4.6 (3.57) [a]
	XIV	4.32, (3.02, 3.72, 4.08), 4.45	4.32 (3.4-3.5)[a]

Table 5 (continued)

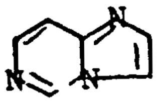
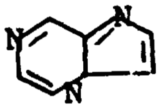
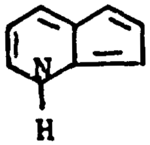
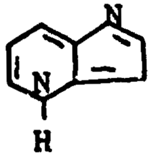
Azaindolizines			
	XVII	3.94, (2.62, 3.23, 3.73), 4.38	3.65 [b]
	XVIII	3.95, (2.70, 3.23, 3.40)	3.78 [b]
Aza-1-pyrindines			
	IX	2.26, (1.35, 2.00), 3.25	2.27 [c]
	XIX	2.46, (1.39, 2.27), 3.44	

Table 5 (continued)

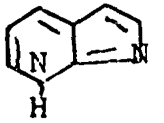
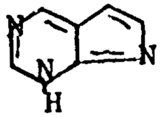
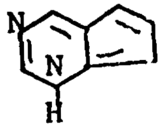
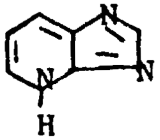
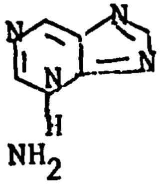
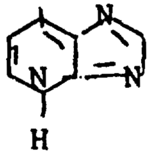
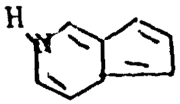
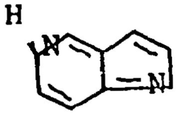
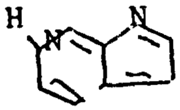
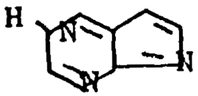
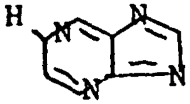
	XX	2.70, (1.76, 2.23), 3.66	2.70[a]
	XXI	2.92, (1.86, 2.67), 3.84	
	XXII	2.58, (1.65, 2.21), 3.40)	
	XXIII	3.73, (2.06, 3.04, 3.56), 3.95	
	XXIV	3.87, (2.28, 3.30, 3.67), 4.18	4.2 [d]
	XXV	3.44, (1.95, 3.44), 4.28	4.0 [d]

Table 5 (continued)

Aza-2-pyrindines			
	X	2.48, (1.48, 2.22, 2.62), 3.28	2.5
	XXVI	2.77, (1.87, 2.45, 2.98), 3.67	
	XXVII	3.06, (1.84, 2.40, 2.93), 3.71	
	XXVIII	2.68, (1.72, 2.56), 4.00	
	XXIX	3.81, (2.31, 3.23, 3.71), 4.38	

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[a] See Table 3.

[b] W. L. F. Armarego, J. Chem. Soc. (London) 4226 (1964), 2778 (1965)

[c] Same reference as for compound XII, Table 3.

[d] L. R. Townsend and R. K. Rabins, J. Heter. Chem., 3341 (1966).

B. C. Pal and C. A. Horton, J. Chem. Soc., 400 (1964).

B. C. Pol, Biochem. 1, 558 (1962).

L. B. Townsend, R. K. Robins, E. N. Loeppky and N. J. Leonard, J. Am. Chem. Soc., 86, 5320 (1964).

N. J. Leonard, J. Am. Chem. Soc., 86, 5340 (1964).

E. P. Lira, J. Heter. Chem. 6, 955 (1969).

J. A. Montgomery and N. J. Thomas, ibid, 1, 115 (1964).

Possible Photophysical Significance of These Calculations

Before discussing the experimental studies of some of these above materials a few things can be stated.

1. Those materials having large S_2-S_1 energy gaps (1 ev) might exhibit upper state fluorescence. The energy gap[15] in azulene, about 1.7-1.8 ev, is sufficiently large so that this material exhibits fluorescence with a quantum yield of about 3%.[31] It might be anticipated that materials with smaller gaps in the 1 ev region would yield upper state emission with quantum yields reduced by several orders of magnitude (10^{-5}).[32]

2. The mismatching of the singlet and triplet manifolds might reduce the rate constant of intersystem crossing by one or two orders of magnitude (to 10^5-10^6 region versus a "normal" 10^7 for hydrocarbons).[33]

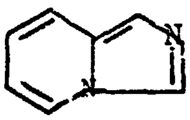
3. Unless geometrical distortions occur in the excited state, as proposed in biphenylene,[34] direct population of the ground state from S_1 will not be important in the materials having high values ofS_1 (possibly above 3 ev) but will be important in the other's low energy S_1 molecules.

4. In those molecules having pyridine type nitrogens there will exist n-pi* states, triplet and singlet, which may strongly influence radiationless processes, especially intersystem crossing. These should only occur, in the 1st order approximation, if the S_1 state is a n-pi* singlet, as it does in the case of purine in hydrocarbon solvents.[36]

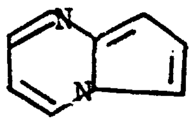
The first thing that should be stressed with regard to physical process is that those processes are extremely complex in molecules like indole, purine, and adenine.[37,38] In the latter two materials most of the energy which goes into the S_1 state is dissipated by unknown processes.[38] Radiative processes are of low quantum yield and over 70% of the absorbed quanta are unaccounted for. In indole itself a complete accounting of the radiative and non-radiative processes has not been reported even in hydrocarbon solvents. The situation in water is even more complex, with the possibility of photoionization.[40]

3. Experimental Studies in Photophysical Processes in Indolizine and Some Azaindolizine

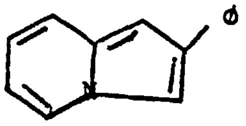
Photophysical studies were initiated in a series of 6 molecules. These were indolizine (XI), 1-azaindolizine (XV), 2-azaindolizine (XXX), 1,8-diazaindolizine (XXXI), 2-phenylindolizine (XXXII), and 2-phenyl-1-azaindolizine (XXXIII).



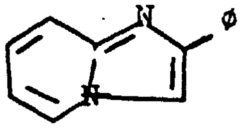
XXX



XXXI



XXXII



XXXIII

Synthesis Compounds XV, XXXII, and XXXIII were obtained from Aldrich Chemical Company. Purification of XV was affected by vpc distillation. XXXII and XXXIII were purified by recrystallization from ethanol followed by sublimation.

The syntheses of XI, XXX, XXXI were effected by standard literature procedures.[41] The physical constants were identical with those in the literature. In addition, the mass spectrum of each material yielded a parent peak of the proper molecular weight. Purification was effected by multiple sublimation immediately prior to use.

Fluorescence Studies Fluorescence studies were carried out using a Hitachi MPF-2A spectrofluorimeter. This instrument can be used in the phosphorescence mode using a light chopping device and appropriate low temperature dewar. Temperature dependence of fluorescence can be followed using a Varian Variable Temperature probe mounted in the unit. Fluorescence lifetimes were determined using a TRW flash system together with lifetime standards of quinine bisulfate crysene and biphenyl.[42] The quantum yield of fluorescence was determined using quinine bisulfate,[43] tryptophan,[44] and PPO[42] as standards, depending on the wavelength of absorption and emission. These materials checked adequately with respect to one another and a separate determination of the quantum yield (Q_f) of fluorescence of anthracene (297K, n-hexane) yielded a value of 0.31, in excellent agreement with the literature value[45] of 0.32.

All the materials studied yielded excitation spectra in agreement with their rather complex absorption spectra and the same emission spectra were obtained regardless of excitation wavelength above 250 nm. In addition, indolizine (XI) is a sufficiently volatile solid to permit the gas phase absorption spectrum to be taken at 297K (10 cm cell). The emission spectra were also recorded at 77K in methylcyclohexane (MCH)-isopentane (IP) as well as EPA glasses. Phosphorescence (77K) was looked for under conditions of strong illumination with and without a phosphoroscope. No emission was detected, instrumentally or visually, for compounds XI, XXX, XXXI, and XXXII, in the 400-600 nm region other than fluorescence.

In Table 6 are shown the room temperature values of the quantum yields of fluorescence in various solvents under conditions which the solutions were air saturated (Q_{O_2}), flushed with nitrogen (Q_{N_2}). Shown also are the respective measured fluorescene lifetimes in nanoseconds.

The major thing that should be noted about Table 6 is the relatively high values for the unquenched fluorescence quantum yields, with all materials having reasonably large values. In particular, the non-phenylated materials all have yields in the 0.7-1.0 region. Although quantum yields this large are in fact not unusual, all of the materials reported in the literature have yields approaching unity have extremely short natural lifetimes, in the [illegible] of 10 nsec.[42] In fact, an examination of [illegible] shows that the materials reported in Table 6 ha[illegible]ue combination of having the largest values of Q_f and longest measured T_f yet reported. Since phosphorescence was only detected in the cases of compounds XV and XXXIII (in the case of XXV the Q_p was estimated as less than 0.01, the emission 0-0 transition occurred at 435 nm with a lifetime of about 5 sec, the corresponding values for XXXIII were 459 nm and 2 sec), it would appear that there is something very unusual about the radiationless processes in these materials. We also tested for photochemical decomposition in the cases of XXI and XXV and found that the quantum yield of photodisapperance in air saturated n-hexane was less than 0.005.

Analysis of the Photophysical Processes

The possible first order rates of a singlet excited state are i) emission, ii) intersystem crossing, iii) internal conversion to the ground state, and iv) photochemical reaction. We have shown that in these materials, i) occurs with high yield, approaching unity, and conversely the others must occur with low yield; that process iv) does not occur in low yields as has been established; that phosphorescence does not occur is indicative that process ii) occurs with virtually no detectable yield. This is not proof, however, since the triplet states of some of these materials might decompose at rates faster than emission rates. This is not true in the case of XXV and XXXIII which have normal phosphorescence lifetimes of 5 and 2 seconds, respectively. In the case of XXV, the yield is low.

The integrated lifetime (natural) for substance XI was calculated from its oscillator strength and found to be in

Table 6

Fluorescence Yields and Lifetimes at 297 K

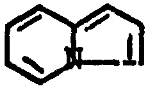
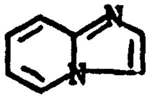
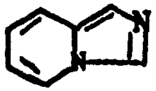
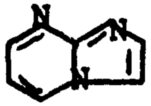
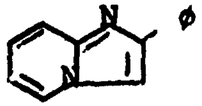
Structure	Solvent	$\overline{\Phi}_{O_2}$	$\overline{\Phi}_{N_2}$	τ_{O_2} (nsec)	τ_{N_2} (nsec)
 XI	h-hexane	0.14	0.84	8	42.4
	methanol	0.22	0.72	12.5	41
	H_2O	0.17	--	15	--
	Gas	0.10	--	--	--
	Glycerol	0.33	--	--	--
	E.P.A.	0.29	0.80		--
 XXV	n-hexane	0.29	0.80	7.5	18.5
	methanol	0.56	1.00	10.5	21
	H_2O	0.16		18.5	
 XYX	n-hexane	0.16	0.98	8	40
	methanol	0.34	0.98	14.8	41.6
	H_2O	0.60	--	30	--
 XXXI	n-hexane	0.43	1.00	9.3	24.6
	methanol	0.51	0.77	15.6	23
	H_2O	0.27	--	2.5	--

Table 6 (Continued)

 XXXII	n-hexane methanol	0.165 0.256	0.60 0.67	6.6 11.2	21.5 28.4
 XXXIII	n-hexane	0.46	0.73	~ 3	~ 6

the order of 40 nsec, almost exactly what is observed, confirming the measured high quantum yield $(Q = T_f/T_n)$. Since the rate constant for photochemical decomposition is negligible the quantum yield for fluorescence can be written as

$$Q_f = \frac{k_f^o}{k_f^o + k_{isc} + k_{ic}}$$

where $k_f^o = 1/T_n$, and k_{isc} and k_{ic} are the rate constants for intersystem crossing (to the triplet manifold) and internal conversion (to the excited vibrational state of the ground electron state). Thus, using $k_f^o = 1/40$ nsec $= 2.5 \times 10^7$ sec^{-1} and a value of 0.8 for Q_f it is computed that k_{isc} and k_{ic} could be in the neighborhood of 5×10^6 sec^{-1}. This would be an upper value for the XI and might even be possibly much less for XXX in which the quantum yield approaches unity. The "normal" range for such a value of intersystem crossing is in the 10^7 sec and higher, with anomalous values running in the 10^5-10^6 region.[33] Thus these materials are in fact anomalous.

The fact that the Q_f are high at room temperature establishes that the materials don't have a temperature dependence to the Q_f. The contrary is true for a number of molecules (pyrene,[46] napthalene,[47] ovalene,[48] and a number of anthracenes).[49] In these cases the rate constant for k_{isc} is temperature dependent resulting in a low degree of intersystem crossing at 77K but much higher at 300K. In the case of pyrene k_{isc} at low temperature is estimated to be in the 10^5 region, or possibly less.[46]

The common sighted reason for the temperature dependence of i_{isc} is to claim that there exists a nearly adjacent triplet state slightly higher in energy than S_1 and, thus, a thermally activated process is needed to occupy the energetically nearest triplet.[50] Although theoretical calculations[51] tend to support such an hypothesis the rationalization seems a bit too convenient considering the large variety of materials which have been shown to exhibit this property. Even so, in our materials the theoretical calculations do show a bad mismatching of the position of the triplet and singlet states. This is to be contrasted with polyacences and (perhaps) derivatives thereof, in which the ^1L_b state is theoretically degenerate with the corresponding ^3L_b (no singlet-triplet splitting occurring) or the lowest excited state of the polyacence is ^1L_a but there is a nearly isoenergetic degeneracy with the ^1L_b state.[52] The former situation applies in the case of pyrene, the latter in the case of anthracene.[53]

On the other hand, it may not be the position of the adjacent triplet state which effects the rate of the $S_1 \rightarrow T_n$ process. In fact we are not entirely sure that a singlet to a particular triplet process actually occurs. No experimental evidence supports it in the literature. It could be that the true process is the $S_1 \rightarrow T_1$ process, which then would be energy gap dependent. In fact no deuterium effect is noted for this process which is known[54] to retard the $T_1 \rightarrow S_0$ process. In this case the energy gaps are large. Conditions under which intersystem crossing would be effected by deuterium effect.[55] Normally, the S_1-T_1 gaps are small and small gaps are not thought to be deuterium dependent.[15,32] What might actually be the case is that the coupling of the S_1 state with the triplet manifold which is dependent on the Franck-Condon overlap factors is a function of <u>all</u> the triplet states which lie, energetically, between S_1 and T_1 as well as the position of T_1 itself.

In fact, too little experimental information is known to give weight to any of these factors.

Solvent Effects on the Absorption and Emission Spectra of These Materials

Indole, the isomer of indolizine, shows some unusual as yet incompletely analyzed solvent-spectral effects.[57] Although it is claimed that the absorption spectra of indole is essentially unchanged in various media this in fact is not so.[58] Konev[58] reports the spectra of indole in hydrocarbon solvent as a function of the addition of small amounts of alcohol. The changes are gradual in that system and appears to be an isopiestic point indicating a distinct complex between indole and alcohol in the <u>ground state</u>. It has long been known that the <u>emission</u> of indole in water and hydrocarbon-alcohol mixtures is relatively structureless.[59] Analysis of this data indicates the formation of distinct indole-alcohol complexes in the excited state (exciplexes).[59] In pure water or pure alcohol the situation may be more complicated in that now the exciplexes themselves can be solvated. In any case the emission in pure hydrobonding solvents is structureless. However the electronic structure of indole is complicated by what appears to be two close lying excited states, S_2 and S_1.[60] It is theorized[61] that solvation causes an inversion in these excited states so that even if S_1 is the original excited state the molecule relaxes, after complex formation (or solvation) to the S_2-solvated state, from which emission occurs. The evidence for this lies in the unusual fluorescence polarization data[61] in alcoholic solvents (frozen EPA) which behaves contrary to that usually observed. In the usual case exposing the sample to polarized light in the spectral region at the red edge of the lowest singlet-singlet absorption (into the S_1 state) yields a strongly positive polarization (in frozen media) near the theoretical limit of 0.5, usually in the 0.3-0.5 region. Indole, however, shows a dip in this region in EPA indicating that the actual emitting species (complexed indole) is throwing off light in a different direction, or that the S_2 state is emitting. In addition, some evidence indicates dual emission, that is, two types of emission are coming from frozen indole solutions. One hypothesis is that indole can emit either from the S_2 or S_1 state, this being true dual emission generated by a slow rate of the S_2 to S_1 internal conversion, which is possible in systems having either extremely large or very small S_2-S_1 energy gaps, <u>or</u> that in frozen solutions indole can exist in <u>at least</u> two different environments and thus emission can be seen from either.

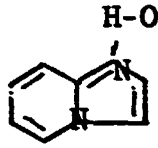
Indolizine provides a convenient test model for examining what might have gone on in such systems. First it is isomeric with indole, but a very large gap of about 8000 cm^{-1} exists between S_2 and S_1, much too large to be perturbed into near degeneracy by solvent effects. Thus exciplex effects will be free from this conflicting complication which exists in the indole case. In addition the polarization can be studied.

An example of the exciplex emission of indolizine is shown in Figure 4 for the solvent plycerol as a function of temperature. At high temperature the emission of XI is virtually structureless but with decreasing temperature the structure shows up, as well as the quantum yield of emission increases. A plot of $\log(Q_f^{-1})$ vs. 1/T yields a straight line with an activation parameter of 3.6 kcals (Figure 5). The corresponding activated process in water for indole is about 3 times higher.[62] In this latter case the process has been attributed to photoejection of an electron. Indeed, with indolizine, the fluorescence quantum yields in water and glycerol are much lower than in methanol or hydrocarbon solvents. The reason for this is not clear. Even in indole, however, the fate of the excited singlet in water is not completely clear.[40] It has not been established what percentage of the excited singlets of indole undergo intersystem crossing, internal conversion, or photochemical reaction (including photoejection). Obviously, even the well studied case of indole (or its near relative tryptophan) has not worked out. In indole virtually no temperature dependence of fluorescence is observed in methanol, while in water the effect is strong. Indolizine has a low activation energy in glycerol. The reasons for this activation energy are still unclear.

Next, unlike indole, indolizine shows no anomalous fluorescence polarization (Figure 6), in EPA or hydrocarbon glasses. The Figure 3 shown covers 2 electronic transitions, the $S_2 \leftarrow S_0$ excitation occurring in the 300-270 nm region, and the $S_1 \leftarrow S_0$ excitation occurring in the 385-300 region. The polarization in the 380 region (0.4-0.5) approaches the theoretical limit of 0.5. The difference between the value of about 0.3 for the $S_2 \leftarrow S_0$ absorption and 0.45 for the $S_1 \leftarrow S_0$ absorption is a direct measure of the difference in the transition moments for these two transitions. The important thing is that indolizine shows no anomalous polarization in the 380 region, indicating that indole is really a separate case, and tends to support the previous interpretation that indole is undergoing some sort of "duel" emission.

Excited State pK_a Effects

However, it must be stressed that the situation for the excited states of the indolizines and azaindolizines are much different than with indole. First, it is noted that the absorption spectra of these materials in hydrogen bonding solvents is completely structureless, indicating a solvated state. This is also the case for the emission at room temperature, but as shown in Figure 4, indolizine exhibits some resolution of structure with decreasing temperature. The 1-azaindolizine is also a case in point. In Figure 7 is shown the absorption spectra of this material in n-hexane plus progressive small additions of n-butanol (1-2% region). A progressive decrease in the 0-0 band is observed, indicating complexation of the heterocyclic by the alcohol, presumably in the form of a hydrogen bond of this type. However (not shown here) the shape and intensities of the entire emission spectrum does not change at all in this concentration region, indicating that the same species is emitting in alcoholic-n-hexane as in n-hexane. The interpretation of these results indicates that the heterocyclic is decomplexing in the excited state in a time much faster than the fluorescence lifetime. This is to be contrasted to the case of indole in which the excited indole undergoes complexation. The question is why?



The actual structure of the hydrogen bonded complex of indole in either the ground state (it exists) or excited is open to question. Presumably it is some sort of pi-bonded complex. In aza-indolizines it is more likely that the complex is directly connected to the n-bonding electrons of the pyridine-type nitrogen atom. Thus, it seems likely that the degree of hydrogen bonding in either the ground or excited state of the azaindolizines is directly related to the ground and excited state pKa's of these materials. Therefore we attempted to measure these.

There are two different methods by which the difference between the ground and excited state pKa's can be estimated.[63] First, an estimate can be made by measuring the absorption spectra of the bases and conjugate acids and together with the experimental ground state pKa's the excited state pKa's can be computed. Or, the absorption and fluorescence spectra of a particular molecule can be measured as a function of pH. A complete estimate using this latter method requires complete relaxation of the molecule within the lifetime of the excited state; a condition which we will show *does not hold* for indolizine.

An estimate of the excited state pK_a (pK_e^*) can be obtained if one knows the ground state pK_a (pK_G) and the absorption spectra of the base (B) and its conjugate acid (BH^+). However, molecules may undergo considerable excited state relaxation and knowledge of the emission spectra may

$$\begin{tikzcd}
B^* + H^+ \arrow[r, shift left, ""] \arrow[r, leftarrow, shift right, "\varepsilon"'] & {}^*BH^+ \\
B + H^+ \arrow[u, "h\nu_1"] \arrow[r, shift left] \arrow[r, leftarrow, shift right, "G"'] & BH^+ \arrow[u, "h\nu_2"']
\end{tikzcd}$$

be required. In the above energy cycle knowledge of any three of the quantities G, ε, $h\nu_1$, and $h\nu_2$ will give the fourth

$$\Delta p_{K_a} = pK_\varepsilon^* - pK_G \simeq \frac{h\nu_1 - h\nu_2}{2.303\ RT}$$

where

$$K_G = \frac{(BH^+)}{(B)(H^+)} \quad \text{and } K_\varepsilon^* = \frac{(^*BH^+)}{(B^*)(H^+)}$$

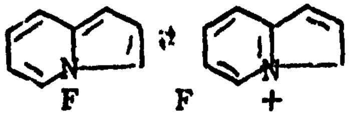
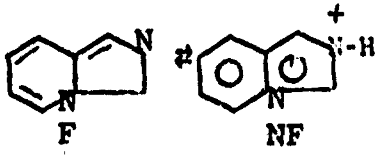
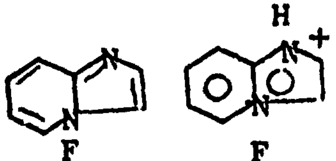
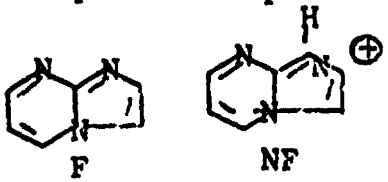
Assuming that the entropy of ionizations in the ground and excited state are equivalent the difference between the ground and excited state pK_a's is given by the above expression. More qualitatively it can merely be stated that if the energy of excitation of the BH^+ specie is greater than the base B the specie will be more acidic in the excited state than the ground state.

As shown in Table 7 this is true for the protonated forms of bases XXI, XXV, XXX, and XXXI. In fact a general survey of the literature[64] shows that all protonated azaindolizines have spectra which are considerably blue shifted with respect to the free bases. The shifts vary but run from 4-10 pK_a units. Since the pK_a's of most azaindolizines run in the 4-6 region it means that in the excited states these materials have pK_a's in the 0 region, or lower, and thus fairly strong acids. This is strongly contrasted from identical cases in molecules like acridine[65] in which the basicity increases in the singlet excited state.

Actual measurement of the excited state pK_a's of these molecules produces the results shown in Table 7. Only in the case of XV was a clearcut excited state pK_a obtained by measuring the emission as a function of pH, the measured value of +0.7 agreeing quite well with that calculated from the spectra, in this case both the B and BH^+ form fluoresce. In both XXX and XXXI, neither of the BH^+ forms gave significant fluorescence. In the case of compound XXXI, an analysis of the pH-fluorescence indicated that the gradual increase in emission in the pH 0 to 4 region was due to increasing amount of ground state XXXI in solution and thus an excited state pK_a could not be obtained. With XXX the same analy is indicated that indeed the excited state BH^+ was responsible for emission in solution of the B form but that the BH^+ form itself was virtually non-fluorescence. This makes the analysis of this data somewhat questionable since although BH^+ excited state doesn't live long enough to emit, it can be deprotonated quickly enough to emit in the form B excited. This would require an extremely rapid rate of deprotonation, possibly in the 10^{11} sec region since the lifetime of XXX is in the 10^{8} region.

Finally, a most unusual result was obtained in indolizine. Although both the acid and base forms fluoresce, prompt fluorescence of $^*B$ resulting from deprotonation of $^*BH^+$ did not occur in the pH 0-3 region even though it is calculated that the $pK_a^* = -6.4$, an extremely strong acid which would be

Table 7
Ground and Excited State (Singlet) pK_a's

Structure $B + H^+ \rightleftarrows BH^+$	$S_0 \rightarrow S_1$ (nm) B	BH^+	pK_a	pK_a^* Calcd. (Spectra)	pK_a^* Obs.
	390	327	3.94	- 6.7	--
	374	340	5.54	- 5.54	+ 1.1*
	333	301	6.79	+ 0.2	+ 0.7
	373	340	4.81	- 0.7	--

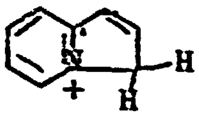
F = specie is fluorescent

NF = specie is non-fluorescent

* = estimated

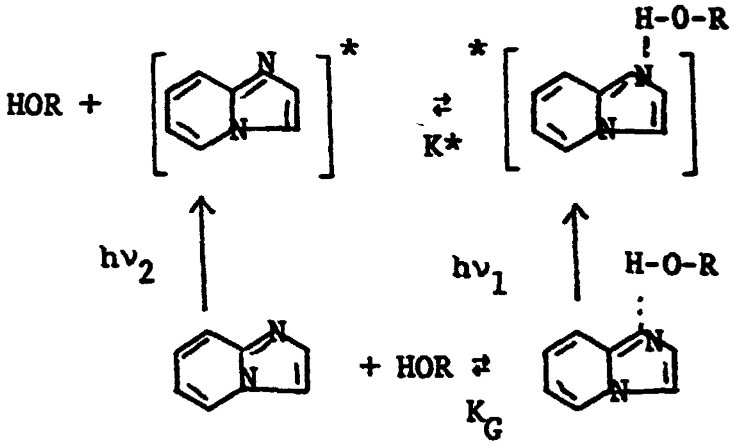
$S_0 \rightarrow S_1$: Located at crossing point of fluorescence and absorption if specie emits; if not, assigned in the red-edge of the absorption bond.

expected to deprotonate at diffusion control rates <u>if</u> BH^+ were an oxygen or nitrogen acid. But it is not, the ground state acid form being



This is what is referred to as a carbon acid and the literature shows that the rates of the deprotonation of carbon acids can be supressed up to a factor of 10^6 below diffusion controlled rates.[66] Since the lifetime of this species is probably in the 10^{-9} to 10^{-8} sec region, and diffusion controlled rates are in the 10^{10} region, the rate of deprotonation of this species could be in the 10^5 region which is at least 1000 longer than the fluorescence lifetime. Thus it is conceivable that the excited state of BH^+ for indolizine just doesn't live long enough to deprotonate. This is consistent with what is observed.

Returning to the problem of XXV the reason why it emits in the non-hydrogen-bonded form although absorption in that form (in n-hexane-butanol mixtures) is apparently related to the gross non-basicity of the nitrogen non-bonded electrons in the excited state. Thus in the equation as follows,



There is a blue shift on formation of the hydrogen bonded material ($h\nu_1 > h\nu_2$). This is what apparently occurs with the observed rapid drop in the apparent 0-0 band XXV (shown in Figure 7.) Thus if $h\nu_1 > h\nu_2$, then $K_G > K^*$, thus the material tends to break hydrogen bonds in the excited state.

Conclusion: These studies, having been just initiated, generate more questions than they answer. The first major question deals with what is the rate of intersystem crossing in the indolizines? Is this the major reason why Q_F values are so high? If so, why? Are the singlet and triplet manifolds really energetically mismatched?

SECTION C PHOTOPHYSICAL AND PHOTOCHEMICAL PROCESSES IN ARENEDIAZONIUM SALTS

Theoretical Considerations Our previous work[67] on the photophysical and photochemical processes have established the following reaction scheme for the arenediazonium salts.

I. Excitation

a. $ArN_2^+ + h\nu \rightarrow {}^1ArN_2^+$

II. Excited Singlet Processes

a. ${}^1ArN_2^+ \rightarrow ArN_2^+ + h\nu$

b. ${}^1ArN_2^+ \rightarrow ArN_2^+ + \text{heat}$

c. ${}^1ArN_2^+ \rightarrow {}^3ArN_2^+$

d. ${}^1ArN_2^+ \rightarrow I_1$

III. Triplet Processes

a. $^3ArN_2^+ \rightarrow ArN_2^+$ + heat

b. $^3ArN_2^+ \rightarrow ArN_2^+ + h\mu$

c. $^3ArN_2^+ \rightarrow I_2$

IV. Processes of Intermediates

a. I_1 (or I_2) $\rightarrow I_3 \rightarrow I_4 \rightarrow I_n$

b. $I_n \rightarrow$ photoproducts

c. $I_n \rightarrow ArN_2^+$ + heat

A number of p-aminobenzenediazonium derivatives had been investigated[67] and it was found that the quantum yields of photodecomposition were i) in the 0.2-0.6 region; ii) no fluorescence or phosphorescence was observed; and iii) the reaction is unquenched by added halide ions. Finally, the reaction was found to have a quantum yield-wavelength dependence in the major absorption band, which for p-aminobenzenediazonium derivatives lies in the 380 nm region.

The lack of emission, even at low temperature, establishes that the yield for processes IIa and IIIc are essentially zero. In addition, the lack of effect of halide ion on the quantum yield also tends to indicate that any excited state or any intermediate which will return to the ground state of the arenediazonium cation has an extremely short lifetime. The intensity of the major absorption band of these p-amino derivatives indicates that the natural lifetime of the singlet excited states are in the order of 1 nsec, i.e.,

$k_f^o = 1/T_f^o = 10^9\ \text{sec}^{-1}$. We would easily be able to detect a fluorescent quantum yield of 1%. Thus at the extreme limit:

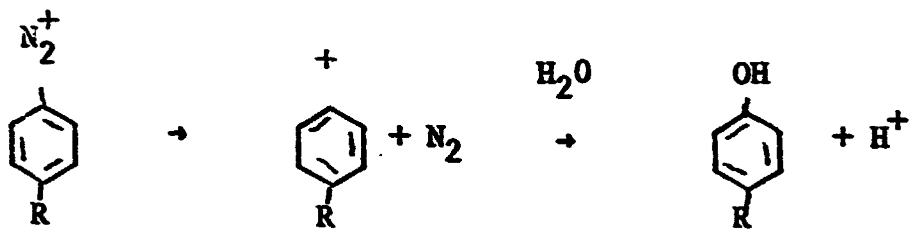
$$Q_f < 0.01 < \frac{k_f^o}{k_f^o + k'}$$

where k' is the sum of the rate processes for all other first order reactions, internal conversion (IIb), intersystem crossing (IIc), and photochemical reaction generating an intermediate. Normal hydrocarbon intersystems crossing occur in the $10^7\ \text{sec}^{-1}$ region[68] and unless spin-orbit factors are operating it seems unlikely that intersystem crossing is competitive in this reaction, i.e., no triplet reactions. We tend to think that the k' is a combination of internal conversion and photochemical reaction rates constants. Thus, if this is so, these processes must be occurring in the 10^{-11} sec region or faster. This is approaching a short of predissociation process which normally only occurs in the gas phase. This may be why the quantum yield is wavelength dependent.

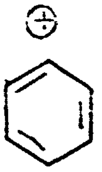
From this view the arenediazonium cation is excited, "immediately" leaves the singlet excited state into some sort of time dependent configuration, part of which returns to the ground state of the arenediazonium cation within 10^{-11} sec, and part of which ends up as some intermediate. The intermediate all ends up as photoproduct(s).

Two main questions arise: i) can this hypothesis be further tested, and ii) what is the nature of the intermediates?

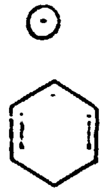
Possible Nature of the Intermediates Thermal chemistry of the aqueous solvolysis of arenediazonium have long proposed the existence of a distinct aryl cation as a reactive intermediate. To this date, however, the existence of such an intermediate has not been established. Conceptually, the following equation does indeed give an aryl cation, analogous to the well-known existence of alkyl cations.



A detailed discussion of the theoretical nature of this possible aryl cation is included in the appendix. The theoretical results are partially ambiguous since they can not be applied to a solvated situation. Nevertheless, the results do suggest the possibility that the aryl cation can exist as either a filled shell singlet, drawn as the localized structure shown below, or as a sort of biradical. The calculations show that either could exist. The photochemical consequences of the existence of these biradical cations



Filled Shell
Singlet



(one resonance form)
singlet or triplet
biradical

are evident by examining the orbital. Symmetry rules for photofragmentation of the arenediazonium salt into the aryl cation plus ground state diatomic nitrogen.

Orbital Symmetry Analysis of the Fragmentation of Arenediazonium Cation to Aryl Cation plus Nitrogen:

Benzenediazonium cation is a planar molecule belonging to the C_{2v} point group, as is the aryl cation as shown above. Simplifying the symmetry properties even further, it can be stated that the orbitals involved in the pi-system are, individually, antisymmetrical to reflection in the plane of symmetry of the molecule, while the sigma orbitals are symmetric. Since the ground state of the benzenediazonium cation is an even electron and filled shell system (every sigma and pi bonding orbital doubly occupied), the electronic state is <u>totally symmetric</u>. The electronically excited states are made up of either pi-pi* or sigma-sigma* excited states. All of these states are symmetric to reflection. However, transitions from sigma to pi* or pi to sigma* orbitals will yield states which are antisymmetric to reflection and therefore belong to a different irreducible representation of the C_{2v} point group than the symmetric states. The same is true for the aryl cation. Assuming now that the diatomic nitrogen molecule departs in its ground state from the arenediazonium cation in a planar fashion, maintaining a planar symmetry for the entire system, the following conclusions can be drawn (see Figure 8).

i) The ground state of ArN_2^+ evolves, adiabatically, into the ground state of the filled shell sigma cation Ar+.

ii) The pi-excited states (singlet and triplet) evolve, adiabatically, into the pi-excited states of the Ar+ ion (singlet and triplet, respectively).

iii) The singlet and triplet biradical forms of the Ar+ ion are adiabatically connected with pi-sigma* and sigma-pi* states of the ArN_2^+.

There is no doubt[69] that the observed lowest energy electronic transitions in the arenediazonium cations are other than strict pi-pi* transitions. Transitions of the sigma-pi* and pi-sigma* type are predicted to be of low intensity and much higher energy than pi-pi* type. Thus, if the ground state of the aryl cation is really biradical, its potential surface must be deeply plunging. In reverse, the potential surface of the process i) must cross the process or ii) surface. This is demonstrated diagramatically in Figure 8.

Experimental Consequences of this type of Potential Surface: The immediate consequence of this type of surface is that the transition state for the thermal decomposition of arenediazonium cations must have some biradical character, in agreement with the analysis of Taft.[70] Since curve crossing as such does not exist in polyatomic cases (vibrational breakdown of symmetry restrictions), it can also be stated that the singlet excited state, S_1 , of the arenediazonium cation is very unstable, since it is connected to the deeply plunging S_n^* state (Figure 8). Thus, a sort of a predissociation takes place. This picture also predicts that there is no return to the arenediazonium ground state, from the reactive intermediates (in this case, S_0'), but there is a branching between this state and the ground state of ArN_2^+ in the region where the 2 potential energy surfaces "cross", this being a "state" S_1'. The closeness of the S_1' and S_0-S_0' surface would yield the prediction that this return to the ground state would occur in the region of 10^{-11} seconds. In addition there are a number of possible experiments that would reject or support this hypothesis. These are:

Experimental Predictions as a Consequence of this Potential Energy Surface

a) Unless $S_0 \rightarrow T_1'$ reaction occurs (or $S_1 \rightarrow T_1'$) the photoproducts should be the same as the thermal products.

b) The photodecomposition by either the singlet or triplet route can be sensitized by singlet (or triplet) materials which have energies between the S_0-S_1 (or S_0-T_1) gap, but above the thermal activation energy (between 30-40 kcal/mole for aqueous solvolysis)[71] for the singlet sensitized process. The products of singlet sensitization would be the same as the thermal or direct singlet excitation process.

c) The photo and thermal reaction products in non-aqueous systems should resemble radical type processes.[72]

d) There is the possibility that if these curves don't cross in the manner shown, the S_1 state may evolve into the excited state of the photoproduct. Because of the strong exothermicity of the thermal reaction,[73] it can be easily shown that there is just enough energy for the excited singlet of ArN_2^+ to evolve into the excited singlet of ArOH (in water), this giving rise to prompt fluorescence from this species. Ironically, in the case of p-amino derivatives of ArN_2^+, this gives rise to a situation where fluorescence would occur at higher energy than the input light generating the photodecomposition.

e) It might be possible to detect the reactive intermediates in flash photolysis. First, in water the attack of water on the species S_0' would be extremely rapid, probably again in the 10^{-11} region, but the T_0' species would be less rapid, or at least the product, triplet ArOH, would have a longer lifetime. In alcohols the possibility of intermediates is already established,[72] although their nature is still unclear but obviously radical products. In particular, the picosecond techniques could actually measure the rate of ground state repopulation, which according to this hypothesis, would be in the picosecond region.

f) The depth of the plunging potential energy surface will be structure dependent with electron donating groups yielding the deepest potential wells. Thus the course of the photophysical and photochemical processes may be strongly substituent dependent. Any study on a particular arenediazonium structure may not yield conclusions applicable to other materials having different substituents.

EXPERIMENTAL STUDIES

Experimental studies were reported[67] on previously on the photodecomposition quantum yields of a series of sterically hindered p-aminobenzenediazonium cations in water. It was found that i) the quantum yields are structurally dependent; ii) wavelength dependent; iii) unquenched in aqueous sodium bromide (2M) solutions; and iv) no emission was detected at 300 or 77K. Recent studies have indicated two things.[73] First, the composition of the products of materials decomposed in aqueous systems are slightly different for the thermal and photochemical decompositions (although these are done at different temperatures). In acidic methanol,[72] the thermal solvolysis reaction products are much different in the presence of oxygen than in the absence. The latter observation is very important since it establishes that different reactive intermediates exist in methanol solution under oxygen than under nitrogen. Therefore several different experiments were carried out. These were, determination of the quantum yields of photodecomposition of p-diethylaminobenzenediazonium cation (DEAD), and p-methoxybenzenediazonium cation (MED) in both water and alcoholic media. The latter material was chosen because of existing data of the thermal decompoistion in methanol and because, since it absorbs at a higher energy, a greater variety of sensitizing agents can be used. Both materials can be used with various laser sources emitting in the 320-350 region. A second series of experiments were carried out preliminary to sensitization reactions to see if the diazonium salts quenched the fluorescence of materials absorbing at much lower energies. Finally, a series of flash experiments were carried out to see if i) what the rate of dissappearance of diazo was; ii) what the rate of appearance of photoproducts is, and iii) if any intermediates could be detected spectroscopically.

I) Quantun yield measurements were carried out using 2 different methods. The first, an adaptation of the continuous monitoring method[74] was discussed in a previous report, requiring the monitoring of the monochromatic light transmitted through the sample as a function of time. At the beginning of a run the sample has a high optical density and the sample is optically clear at the end of a run (no light absorption photoproducts). The time dependence of light transmitted is given by the following equation:

$$\log\left[\frac{I_o}{I_t} - 1\right] = -\sigma Q_p I_0 t + \text{constant}$$

where

Q_p = quantum yield,

I_0 = light intensity striking sample,

I_t = light intensity transmitted at time t,

t = time,

σ = capture cross section.

Thus, if the function $\log_{10}(I_0/I_t - 1)$ is plotted against time, a linear plot will result. The slope of this plot (in $\sec^{-1}$) is $I_0 Q_p \sigma$, where σ is the extinction coefficient in the proper units of cm^2/molecule if the light intensity is in the units of photons/cm^2 sec. This extinction coefficient is essentially the capture cross section, base 10. Classically, extinction coefficients are given in units of liter/mole cm. Thus a molar extinction coefficient of 10,000 liter/mole cm = 10^7 cm^2/mole = 1.7×10^{-17} cm^2/molecule. This is approximately a fifth of a square angstrom, or the order of magnitude expected for the capture of a photon by a molecule. Thus for a molecule having this order of magnitude of a capture cross section, σ, a quantum yield of 0.5, and using a monochromatic light intensity of 10^{15} photons cm^{-2} sec^{-1} the slope would be in the order of 10^{-2} sec^{-1}. A statistical analysis shows that the best region to collect data is in the region where the sample is transmitting between 20-80% of the light. A typical sample having a molar extinction coefficient in the 10,000-40,000 region will decay from 20% to 80% transmission in a matter of 1-3 minutes. In practice, using monochromatic mercury lines, a sample may decompose too quickly for the response of the recorder. On the other hand, non-monochromatic light sources may be too weak and drift problems either with the photomultiplier-recorder or the lamp may make it difficult to record decay curves above 10 minutes.

This technique also requires knowing the light intensity I_0, which can be obtained using standard actinometry. However, the light intensity of mercury arc lamps may vary over several hours (or less). However, once one diazo has been standardized at a particular wavelength, it can be used as a fast actinometer. This was what was done. Classically, the standard ferrioxalate actinometer[25] is somewhat irratic and care must be taken in its application by making a number of runs.

Another method of avoiding the problem of arc lamp drift, and also allowing for exposures at non-mercury line emission in the continuous portion of the emission of the

Xe-Hg lamp used, is to construct a split beam photochemical apparatus in wh[illegible] exposes, simultaneously, both the actinometer and the sample. The construction is simple, only requiring a beam plate having approximately a 50-50 intensity split. The only thing required is to calibrate the plate at a particular wavelength to find how much light goes in each direction, this being accomplished by placing actinometer solutions in both beams. In preceeding runs an actinometer is placed in one beam and the unknown in the other. Analysis of the amount of decomposition in the actinometer allows one to calculate back and find out how many photons hit the unknown solution. If optically dense solutions are used in each case, plus cuvettes of the same transmission characteristics, all reflection light losses cancel and need not be considered.

Both the continuous monitoring technique and beam splitting technique were utilized. In a previous study on DEAD, using the monitoring technique, a yield of 0.50 was found. In this present study a value of 0.46 was found. A list of the quantum yields in various solvents for DEAD and MED are shown in Table 8. In addition the φ_p for MED was tested in aqueous 2M NABr and found to be the same value as listed in Table 8 (0.39). In addition the 0.39 value is in agreement with previous aqueous work (0.38)[71] although previously we found that these authors' value for dimethyl aminobenzenediazonium cation of 0.43 was in disagreement with our value (0.57) as well as other authors (0.58),[75] (0.46),[76] the latter two at 380 nm. The variation of values from literature sources for a number of the same aryldiazonium salts makes us somewhat dubious as to the absolute accuracy not only of other work but our own.

In some respects, the methoxy-derivative is analogous to the dialkylamino derivatives. No emission is detected and no sodium bromide quenching of the decomposition. However, the MED derivative showed much more sensitivity to solvent changes. The quentum yields (Table 8) were higher in alcohols. In air, we detected nothing but a first order decomposition; the same results have not yet been done in N_2 atmosphere. We also found that the aqueous yields were neither concentration or intensity dependent (Table 9). The photoproducts in aerated and nitrogen flushed methanol are reported as follows:[77]

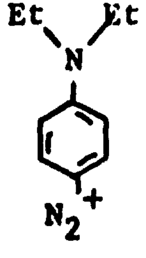
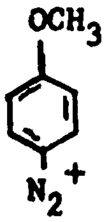
Decomposition of MED in Methanol

Products * % in		
Air (O_2)	8% (4%)	92% (65%)
N_2	74% (73%	26% (11%)

*thermal values given in (72).

Table 8

Quantum Yields of Photodecomposition of Arenediazonium Salts in Various Solvents

Structure	Solvent	λ_{max}	E_{max}	Q_p^* 313 nm	Q_p^* 365 nm
	Water	381	40,000	---	$0.46^a \pm 0.02$
	Methanol	381	40,300	---	0.48^b
	Ethanol	381	40,500	---	0.47^b
(DEAD)					
	Water	313	24,800	$0.39 \pm .01^a$	---
	Methanol	313	21,700	0.54^b	---
	Ethanol	313	22,800	0.47^b	---
	n-Propanol	313	23,600	0.46^b	---
(MED)					

* (in air)

a By beam splitting method, average of 4 or more runs.

b Monitoring method.

Table 9

Q_p as a Function of I_0 for DEAD

I_0 (photons cm^{-2} sec^{-1})	Q_p
3.48×10^{15}	0.46
1.92×10^{15}	0.49
0.87×10^{15}	0.47
0.35×10^{15}	0.50

The values indicate that the product forming stages involve some sort of radical intermediates in the mechanisms for the formation which is killed off under oxygen.[72] In all studies, we have encountered no breakdown of the reciprocity law, that is, no dark reaction taking place after exposure and that exposure could be interrupted and started up again without encountering decomposition of the material in any way other than a first order process. However, we have not yet done this carefully in alcoholic solvents in the strict absence of air. In addition, the photolysis under air free conditions at various concentrations and light intensities should tell us something about any possible chain reaction, which has been proposed to explain the thermal solvolysis results in air free methanol.[72]

Low temperature quantum yield measurements were attempted on DEAD so as to determine if there was any activation energy to the excited state decomposition. Monitoring decay curves were nearly the same at -78C as at 300C and at -114C. In any case we determined that at the outside limit the Q_p was not lower than 0.34 at -114C, the value being 0.46 at 25C. Some difficulty was encountered with the low temperature results with standardizing the light intensity within the low temperature dewar system we were using. The system has been redesigned for future use.

In particular we had difficulty with the systems when the solvent enters the glassy stage, but we have some non-quantitative results which indicated that the rate of decomposition in frozen ethanol is greatly diminished at -196C. Only one author has studied this previously and found no low temperature change in plastic film media, indicating no activation energy to the Q_p.

2) Quenching Experiments Using MED which has an absorption maxima at 313 nm, but little absorption at 365 and virtually none at all at 400 nm, it would be generally predicted that this material could not quench the fluorescence of another material which absorbs at lower energy unless it did so by photooxidizing the material or reacting with its excited state to give a photoproduct. Two classic materials were chosen, the first, rhodamine B, a cationic dye absorbing in the 550 nm region and quinine sulfate (in acid) also a cationic material

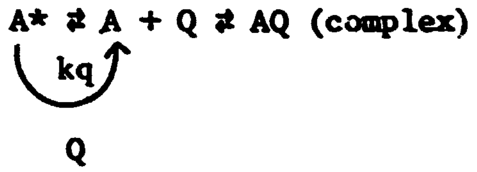
whose absorption characteristics overlap MED but at slightly lower energies. The technique was to plot the quenching of the emission of these materials in separate experiments containing various amounts of MED, and to plot the results in a typical Stern-Volmer manner so as to obtain the quenching constant. Since the fluorescene lifetimes of these two materials are experimentally known,[79] it should be then possible to see what the actual bimolecular quenching constant is, if quenching occurs at all. In fact, two typical quenching plots are shown in Figures 9 and 10.

With quinine sulfate, exposed at 400 nm (the red edge of its absorption band), a quenching slope of 32 $(M)^{-1}$ was obtained. In classical Stern-Volmer analysis this slope is $= T_f \times k_q$, where k_q is the second order rate constant for the reaction.

$$\text{MED} + \text{QS}^* \xrightarrow{k_q} ???$$

Using a T_f for quinine sulfate of 18 nsec this yields a k_q value of 1.8×10^9 cm^{-1} sec. This is fairly close to the diffusion controlled value in water of 4.0×10^9 $\text{mole}^1\text{-sec}^{-1}$.[80]

With rhodamine B a limiting slope of 14.3 m^{-1} was obtained with a calculated k_q of 2.4×10^9, using a lifetime of 6 nsec. As shown in Figure 9, the rhodamine B results show a super linearity to the quenching, the quenching becoming more efficient as the diazo concentration was larger. Such a super linearity sometimes indicates a ground state complex according to the model



so that

$$\frac{I_0}{I} = (1 + KQ)\ (1 + (T_f k_q Q))$$

or

$$= 1 + (K + k_q T_f)(Q) + K k_q T_f\ (Q)^2$$

where I_0, I are the fluorescence intensities, K the complex formation constant (AQ/(A)(Q)), and k_q and T_f have been previously defined. Thus a plot of the quantity $(I_0/I - 1)/Q$ versus Q should give a straight line. This was found in the case of rhodamine B. Further investigation indicated that the counterion of the diazonium salt, BF_4^{-1}, reacted in some unknown fashion with rhodamine B to remove some of it from solution, this giving an artificial decrease in fluorescence intensity (due to the fact that there was less active rhodamine B present). Thus, under this situation it was not the diazonium salt which reacted with rhodamine B to form a"complex" but the BF_4^{-1} ion. In both cases, no rapid reaction of ground state diazonium salt and the fluorescent agent was noted.

In the case of rhodamine B, however, 2 other different reactions were noted. First, a slow dark reaction; solutions of the diazonium salt and rhodamine B decomposed over the course of a week or so with the removal of the latter material. Since the concentrations worked at were roughly 0.1 molar diazo and 10^{-5} rhodamine B, we were not able to detect a decrease in the concentration of the diazo. A rapid removal of the rhodamine B was noted when the solutions were exposed to high light intensities (10^{14} photons cm^{-2} sec^{-1}). Rhodamine B was found to be stable under identical conditions, dark or light, in the absence of the diazonium salt. Thus as a "sensitizer,"rhodamine B is out since it is not stable and will not "turn over" large quantities of diazo. Again, since the concentration range difference between the diazo and the sensitizer were too great, we could not detect disappearance of the diazo when the rhodamine B was either quenched or decomposed. We are presently searching for a sensitizer which will be stable under the conditions of the reaction. Quinine sulfate looks like a promising candidate.

What has been shown is that there is quenching, that somehow the diazonium is either stealing energy or causing internal conversion to take place. If quenching had not occurred our potential surface hypothesis would have been immediately proven wrong.

3) *Flash Photolysis* In principle flash photolysis would allow us to generate large amounts of intermediate material in a short period of time. The best flash would be the shortest flash. However, to date the only unit available was one which yields upto 1000 joules with a complete tailing out (no flash) in about 1000 μsec (or 1 msec). Thus we could only examine species living longer than 10^{-3} sec. Only the most stable intermediates could live this long. We generally found that flashes in the order of 300 joules were enough to decompose a solution having an optical density of 10 in a 10 cm cell. Using a Xe arc lamp plus an input monochromator plus an output double monachromator we could span the optical detection range from about 230 nm to 600 nm. Using DEAD which absorbs at 380 nm and monitoring that wavelength by light traveling through the solution, we found that the diazonium salt disappeared within the *time of the flash*. Nor was there any significant recovery of diazonium optical density in solutions flashed in such a way to reduce the optical density from about 10 to about 0.5 (from optically "black" to transmitting some light). Thus the diazo is all reacting within the time span of the flash and all material *not* reacting, although some or all of it must have been excited, is getting back to the diazonium configuration within 1 msec. Flash samples and slowly exposed samples had the same absorption spectra.

Thus it would appear that diazonium material does not give a metastable species with a longer lifetime than 1 msec. We are also able to monitor the formation of the photoproduct at 223 nm. This is a difficult region to work in and a double monochromator was necessary to "clean" up the light coming through the system. A single monochromator at the same wavelength was found to have about 50% scattered light. In any case the spectra at this position is to the diethylaminophenol ($\epsilon \cong 7{,}000$). Although such a phenol absorbs at a higher wavelength (between 260-300) the extinction coefficient is weak and not enough optical density changes to make detection practical. Virtually no optical density change was detected in this latter region, whereas a significant increase in optical density was detected in the 223 nm region.

In any case we found that the formation of the phenol in this region <u>also</u> occurred in the time span of the flash.

Finally, we monitored the transmission over the range between 400 and 600 nm and found no transients with lifetimes longer than the flash.

Clearly the flash length is too long. Preferably a flash in the nsec region would be better, and in the picosecond region best.

Present Conclusion of the Diazonium Work The initial quantum yield work has been done at 365 and 313 nm. Now we have good actinometers for these two wavelengths. Future work should be done in i) flash photolysis, detection of intermediates in nitrogen flushed alcoholic solutions, where they are known to exist chemically, ii) low temperature photolysis, iii) product analysis in alcoholic solutions, and iv) sensitization, both with singlet and triplet sensitizers, plus quantum yields of decomposition and product analysis in alcoholic solutions.

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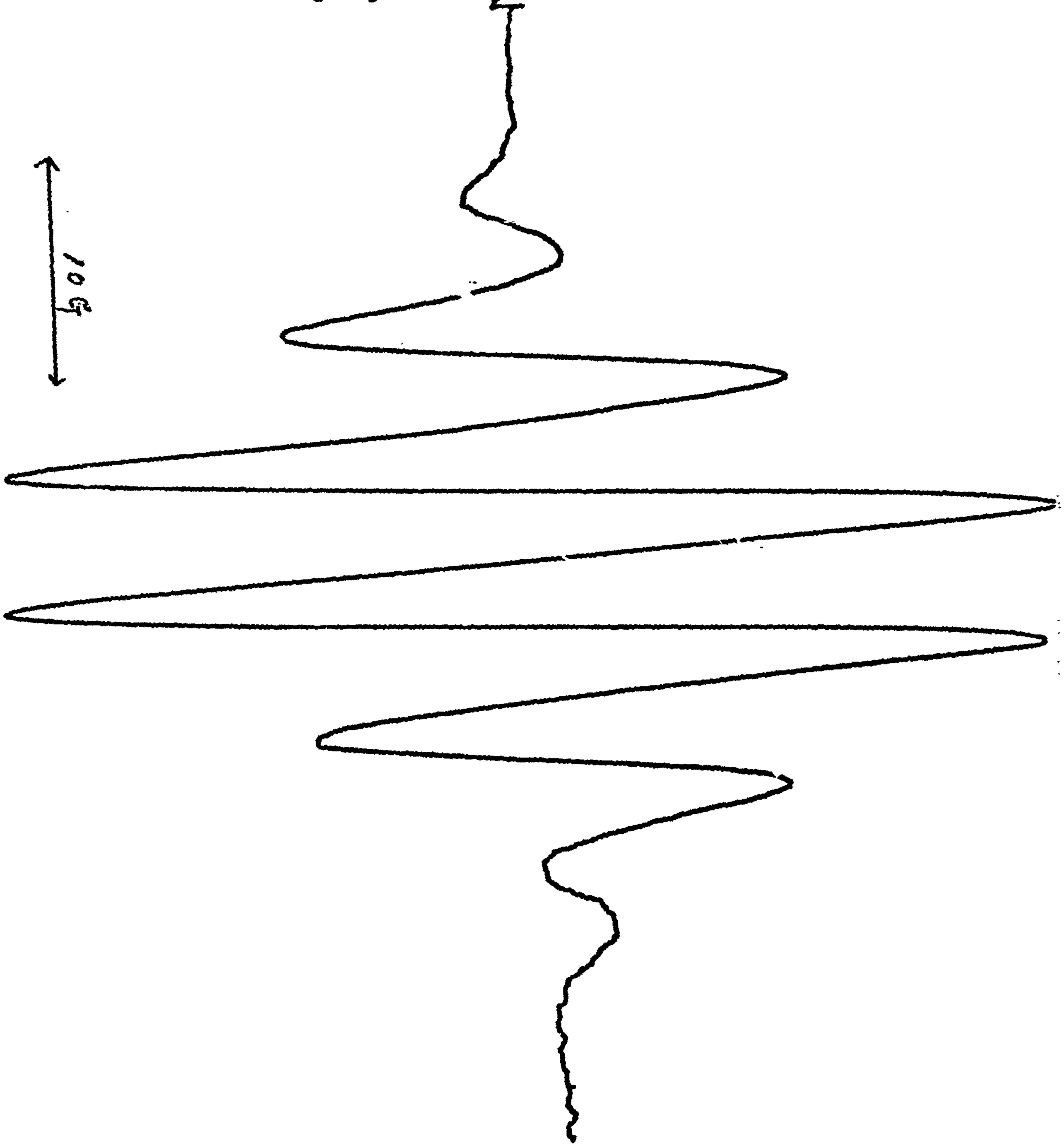
FIGURE 1 cyclopentadienyl radical



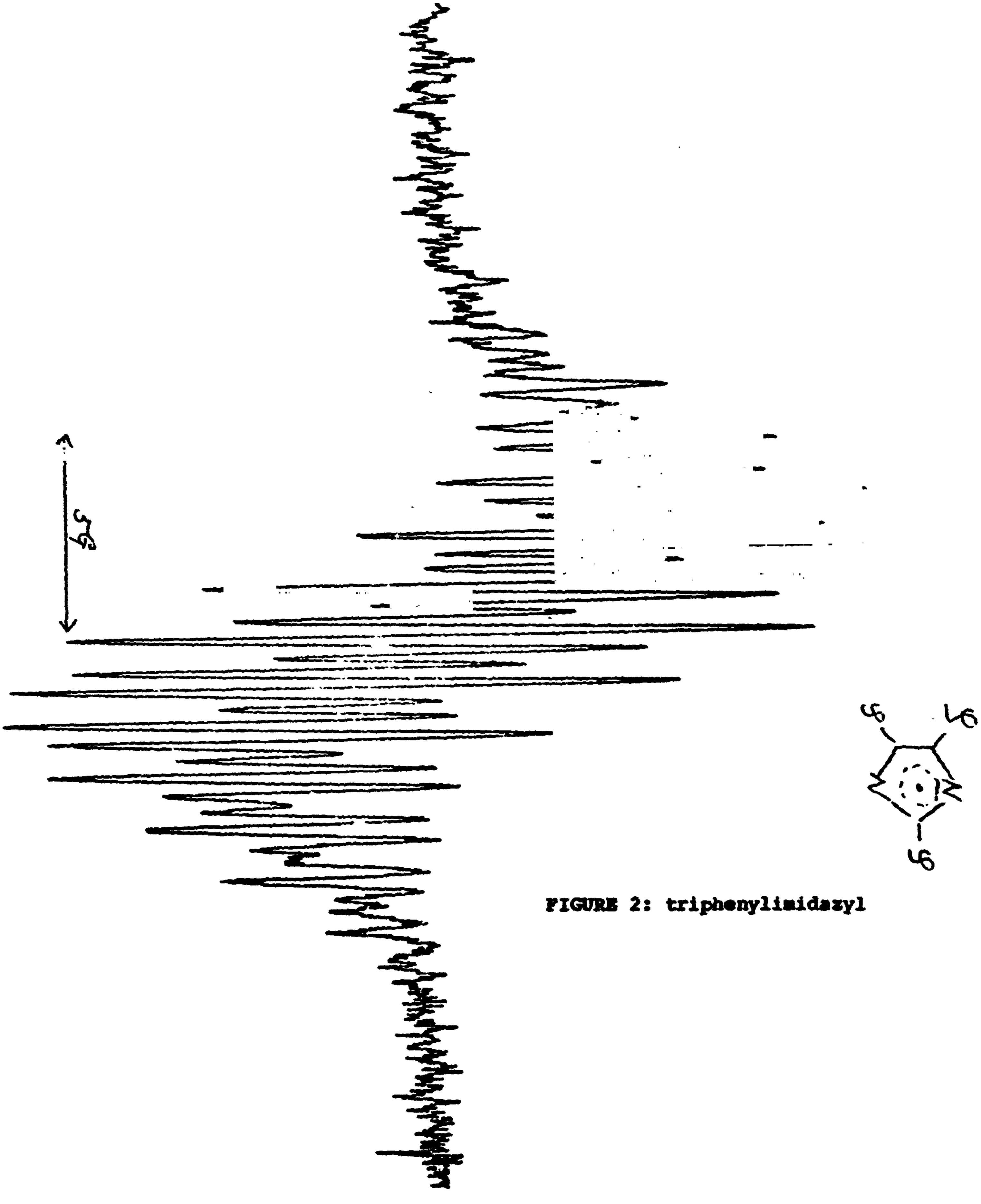
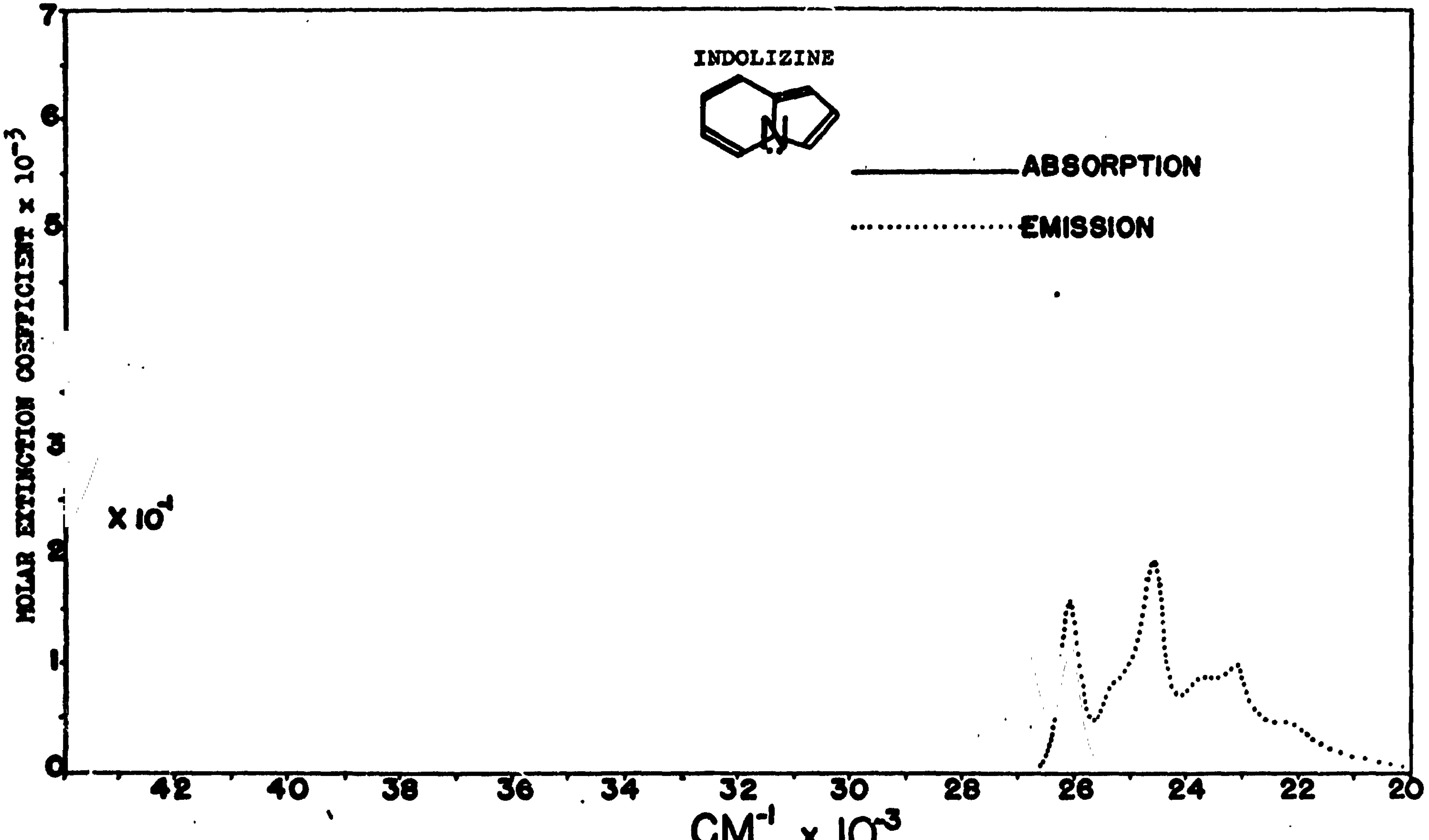


FIGURE 2: triphenylimidazyl



ABSORPTION AND EMISSION SPECTRUM IN HEXANE

FIGURE 3

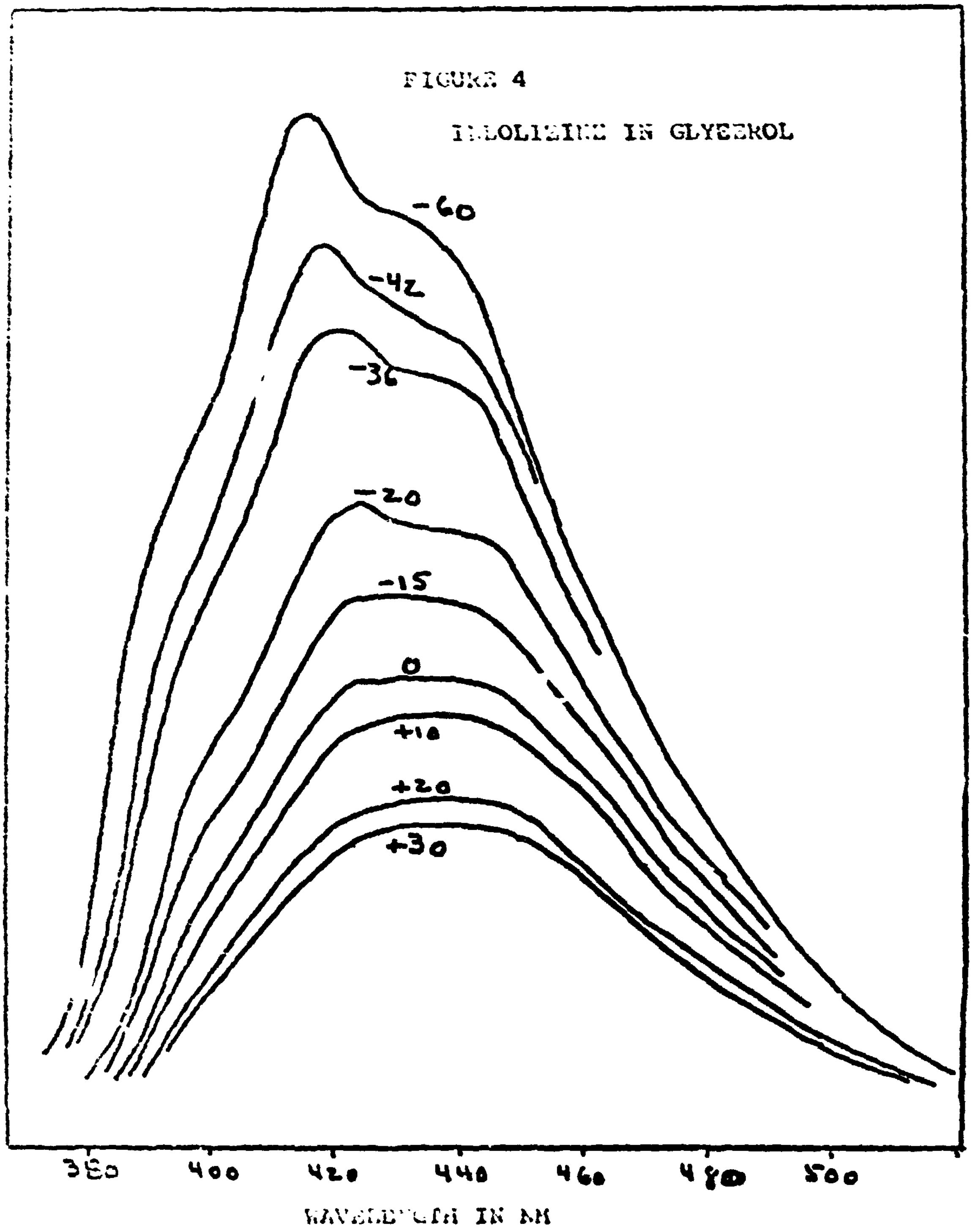


FIGURE 4

INDOLIZINE IN GLYCEROL

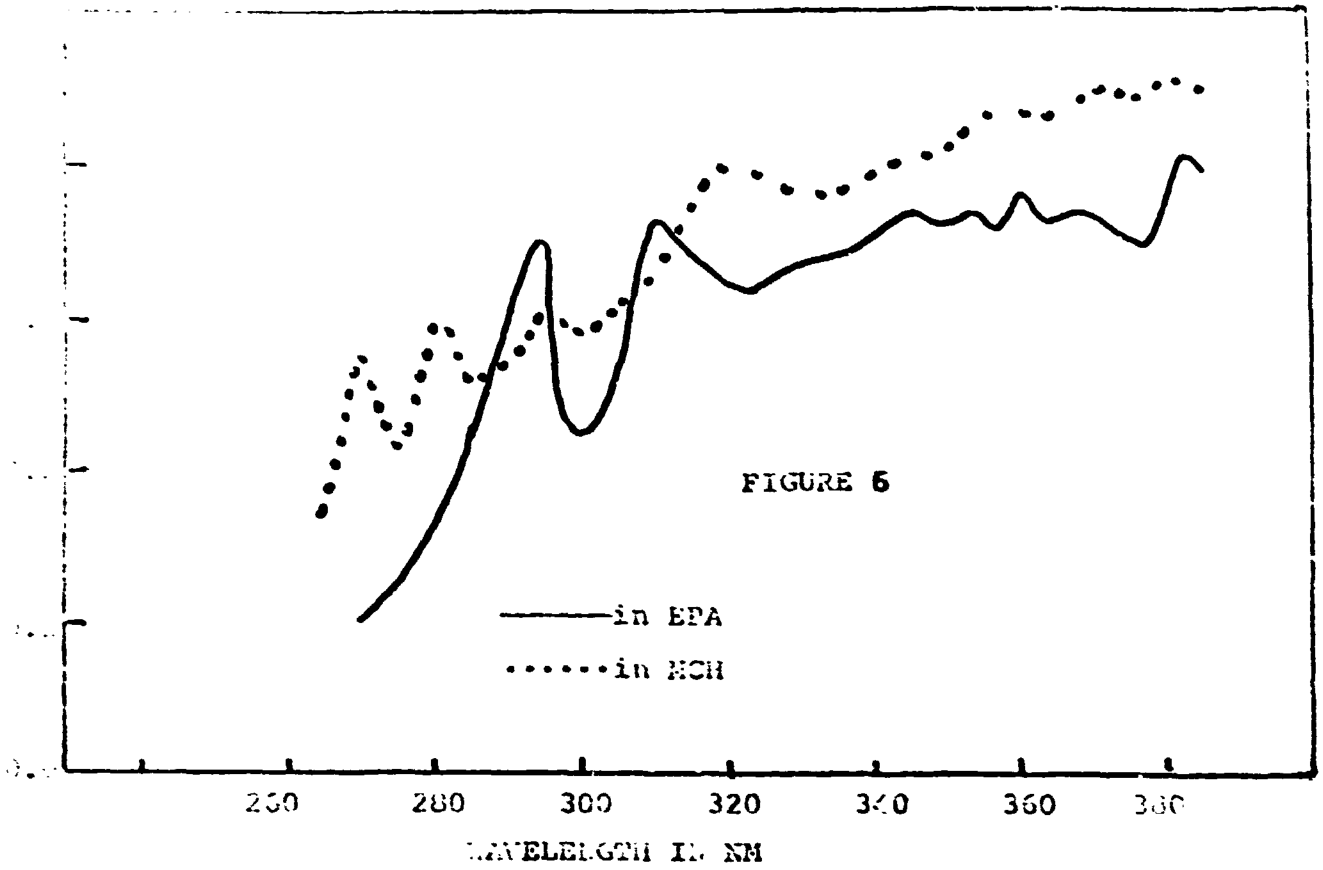


FIGURE 6

POLARIZED [illegible] EXCITATION CURVE OF INDOLIZINE

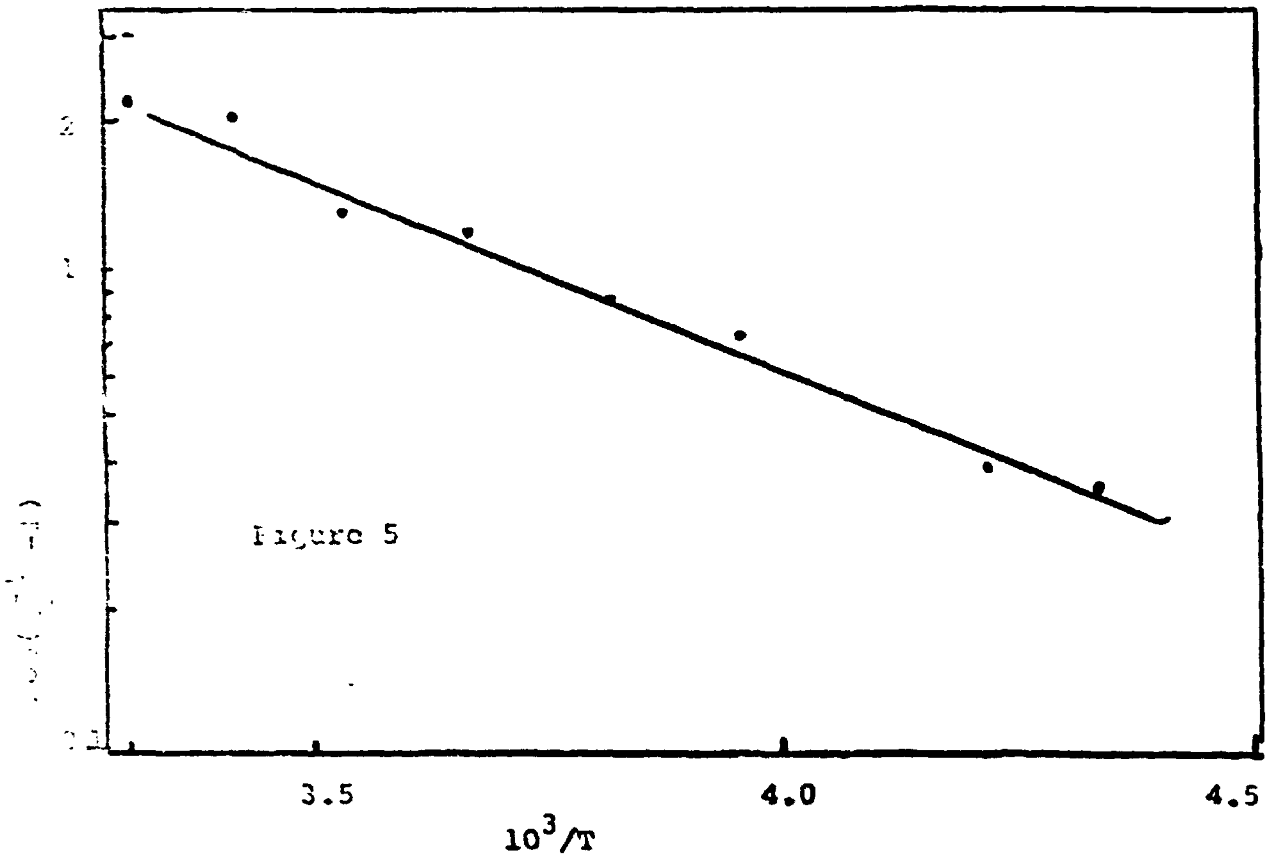


Figure 5

Temperature Dependence of Q_f in Glycerol

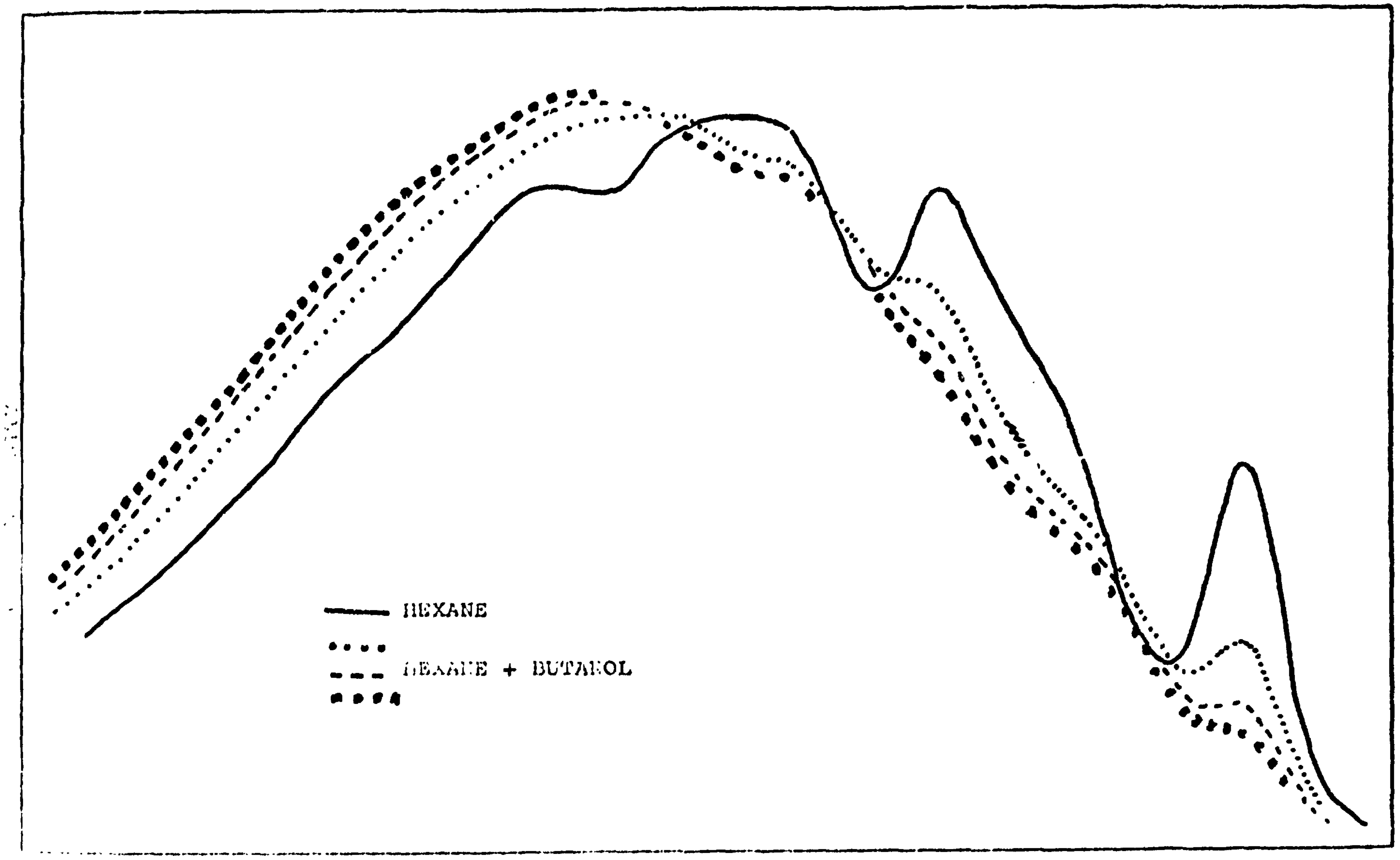
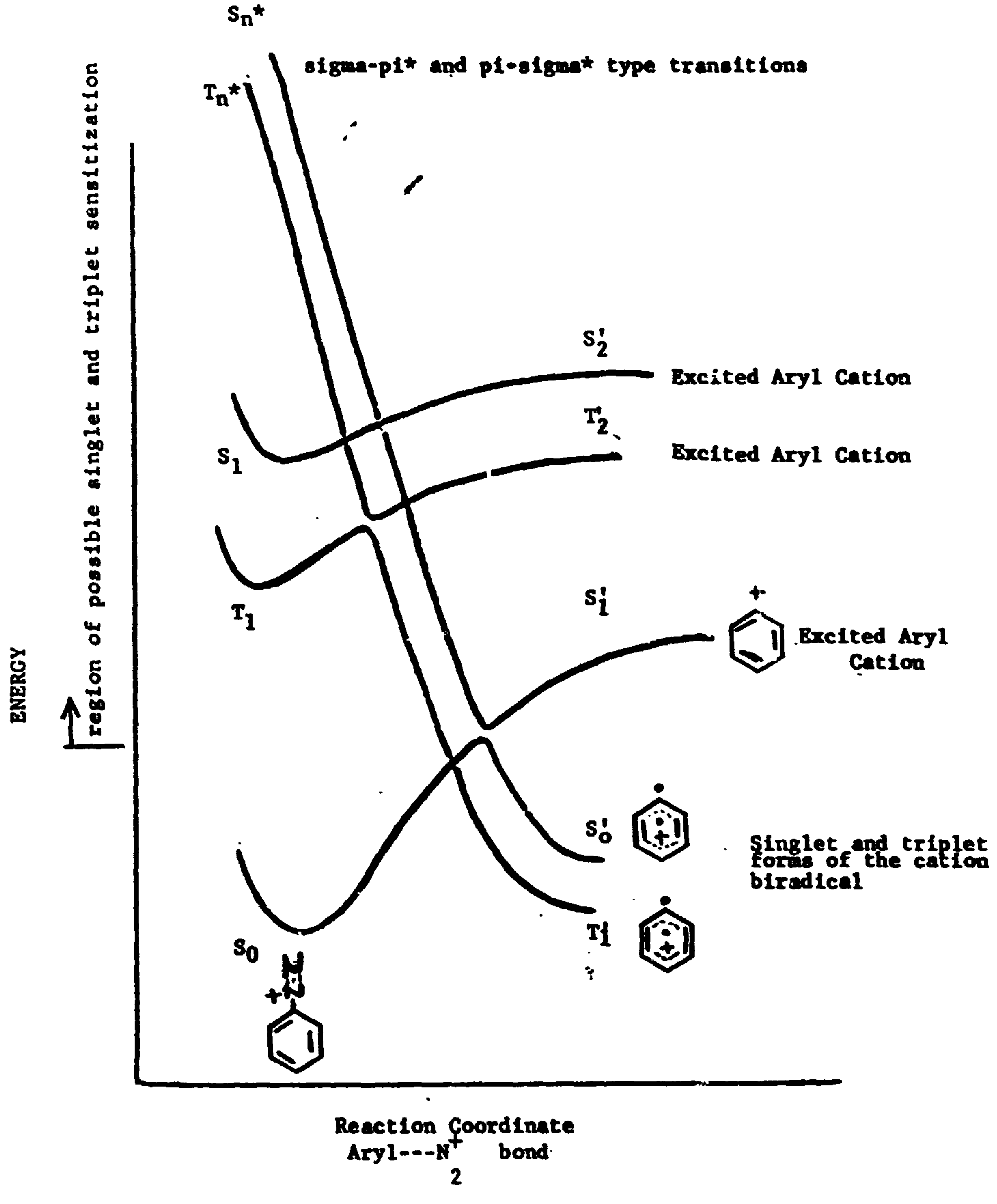


FIGURE 1



S_0 = ground state of aryldiazonium cation

S_1, T_1 = spectroscopic singlet and triplet states of aryldiazonium cation (pi-pi* excited states)

S_n,T_n = hypothetical sigma-pi*, pi-sigma* excited states of aryldiazonium cation

S'_o,T'_1 = "ground" biradical states of the aryl cation

S'_1, S'_2, T'_2 = excited states of the aryl cation

FIGURE 8

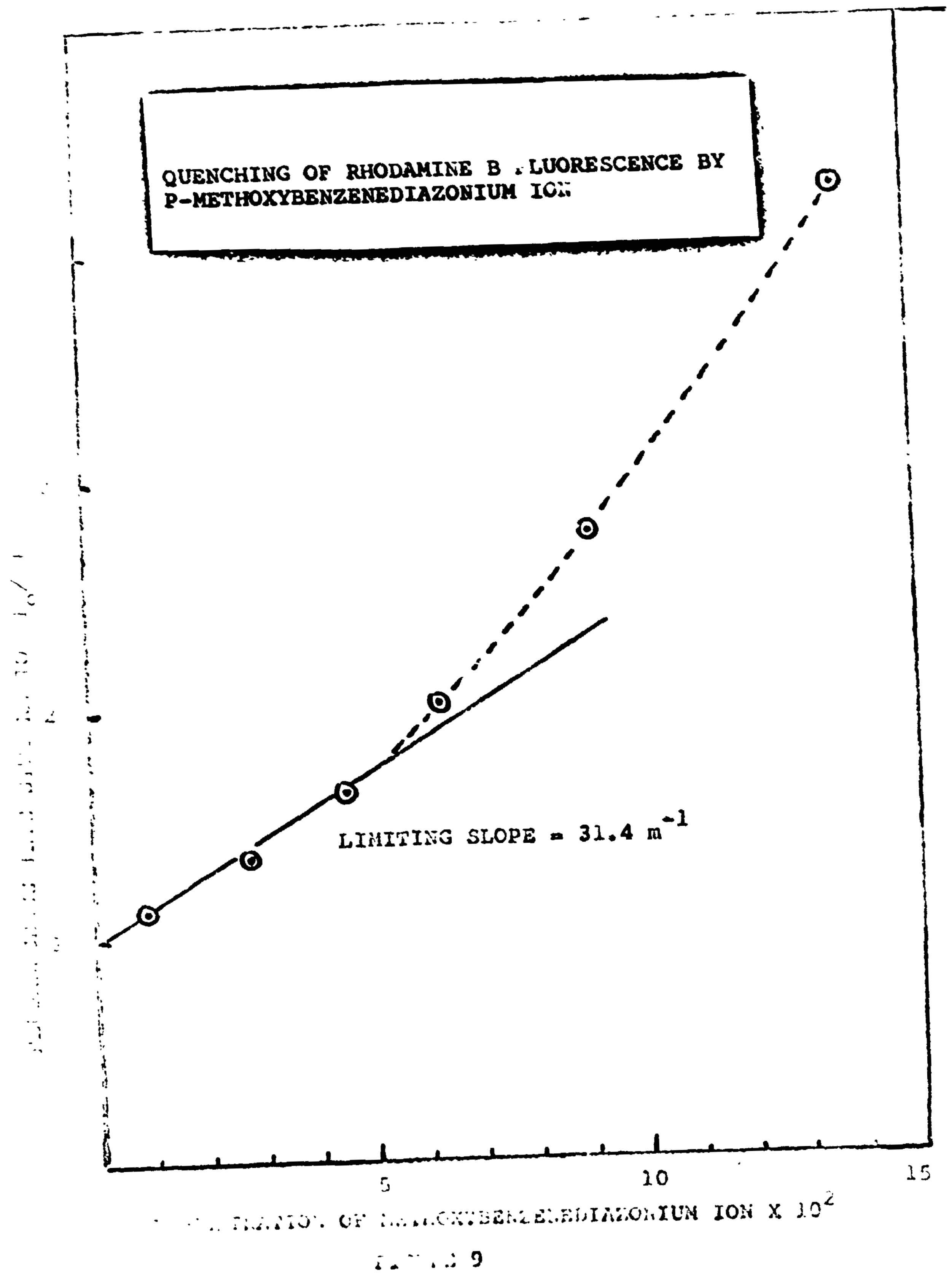
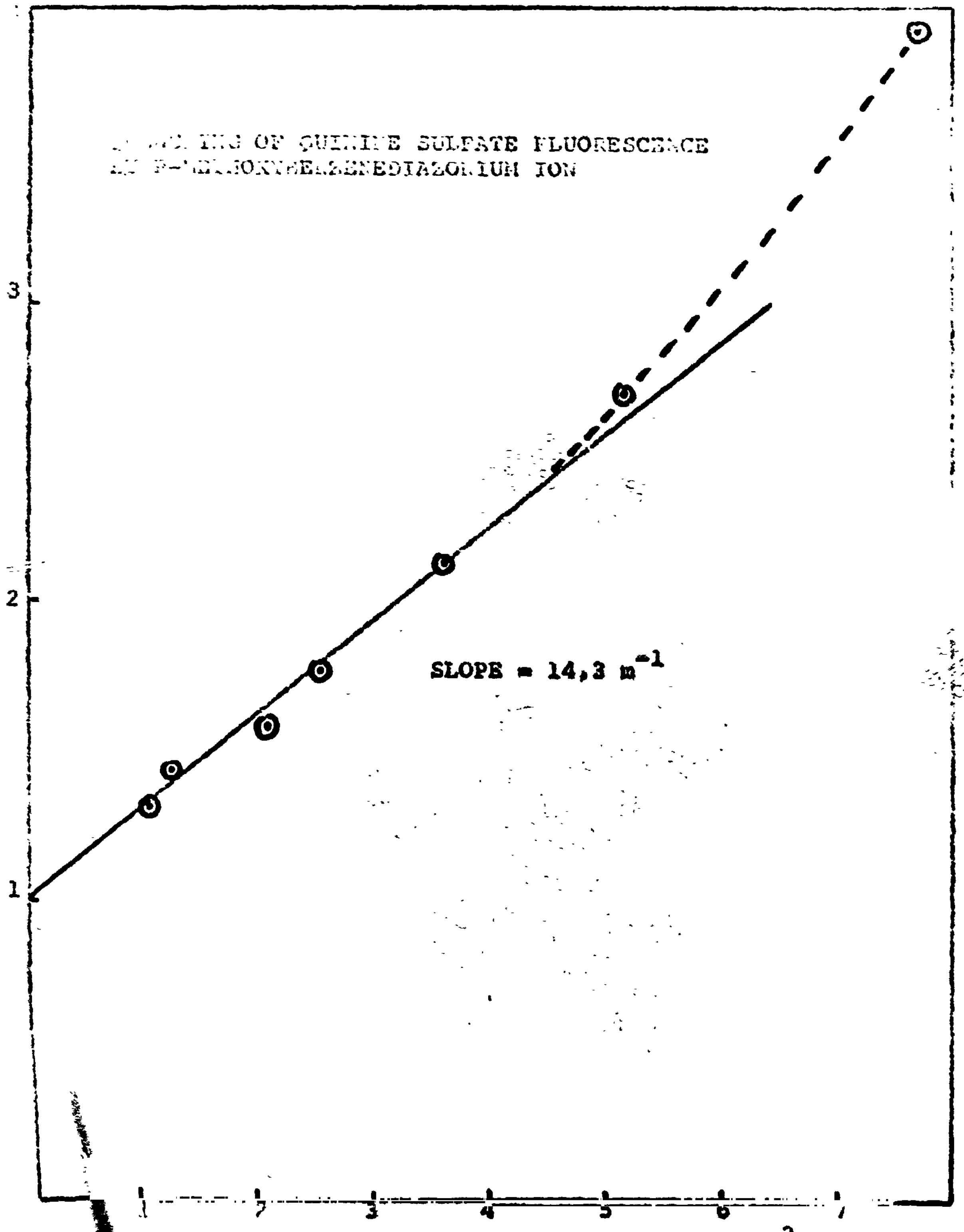

QUENCHING OF RHODAMINE B FLUORESCENCE BY P-METHOXYBENZENEDIAZONIUM ION
LIMITING SLOPE = 31.4 m^{-1}
2
5
10
15
CONCENTRATION OF P-METHOXYBENZENEDIAZONIUM ION X 10^2

FIGURE 9



...ING OF QUININE SULFATE FLUORESCENCE
... P-METHOXYBENZENEDIAZONIUM ION
3
2
1
SLOPE = 14,3 m^{-1}
1
2
3
4
5
6
7
...TRATION OF P-METHOXYBENZENEDIAZONIUM ION X 10^2

FIGURE 10