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The Spectroscopy of Neutral and Ionic Forms of Triphenylformazan Derivatives.

Elizabeth Wilhite

Louisiana State University and Agricultural & Mechanical College

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The spectroscopy of neutral and ionic forms of triphenylformazan derivatives

Wilhite, Elizabeth, Ph.D.
The Louisiana State University and Agricultural and Mechanical Col., 1991
THE SPECTROSCOPY OF NEUTRAL AND IONIC FORMS
OF TRIPHENYLFORMAZAN DERIVATIVES

A Dissertation

Submitted to the Graduate Faculty of the
Louisiana State University and
Agricultural and Mechanical College
in partial fulfillment of the
requirements for the degree of
Doctor of Philosophy

in

The Department of Chemistry

by

Elizabeth Wilhite
B.S., Mississippi University for Women, 1980
May, 1991
In memory of Elizabeth Gilmer Freeman
ACKNOWLEDGMENT

The author wishes to thank her major professor, Robert Nauman, for providing a fertile environment for intellectual growth. His unswerving guidance, patience and respect are deeply appreciated.

The friendship and suggestions of Steve Arnold and Cristian Franco are gratefully acknowledged.

The expertise, advice and patience of Bob Zinn and Marcus Nauman are gratefully acknowledged. The donation of chemicals and equipment by Drs. McGlynn and Daly and the advice of Drs. Kestner, Lewis and Traynham are appreciated.

Toni Bova and her family provided a home away from home for the author. Their love and support are deeply appreciated.

The author wishes to thank her family for their love, faith and support throughout her career. Without them this work would not have been possible.
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<thead>
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<th>Definition</th>
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<tr>
<td>1,3-diphenyl</td>
<td>1,3-diphenylformazan</td>
</tr>
<tr>
<td>1,5-diphenyl</td>
<td>1,5-diphenylformazan</td>
</tr>
<tr>
<td>1-methyl</td>
<td>1-methylformazan</td>
</tr>
<tr>
<td>3-methyl</td>
<td>3-methylformazan</td>
</tr>
<tr>
<td>1-phenyl</td>
<td>1-phenylformazan</td>
</tr>
<tr>
<td>3-phenyl</td>
<td>3-phenylformazan</td>
</tr>
<tr>
<td>ACN</td>
<td>acetonitrile</td>
</tr>
<tr>
<td>Calc.</td>
<td>calculated</td>
</tr>
<tr>
<td>CI</td>
<td>configuration interaction</td>
</tr>
<tr>
<td>CT</td>
<td>charge transfer</td>
</tr>
<tr>
<td>DCM</td>
<td>dichloromethane</td>
</tr>
<tr>
<td>Diform</td>
<td>1,1',5,5'-tetraphenyl-3,3'-(p-biphenylene)-diformazan</td>
</tr>
<tr>
<td>Dimsyl</td>
<td>deprotonated dimethylsulfoxide</td>
</tr>
<tr>
<td>DMF</td>
<td>N,N-dimethylformamide</td>
</tr>
<tr>
<td>DMSO</td>
<td>dimethylsulfoxide</td>
</tr>
<tr>
<td>LDA</td>
<td>lithium diisopropylamide</td>
</tr>
<tr>
<td>m-Br</td>
<td>3-(3-bromophenyl)-1,5-diphenylformazan</td>
</tr>
<tr>
<td>m-Br(^-)</td>
<td>deprotonated m-Br species</td>
</tr>
<tr>
<td>m-BrH(^+)</td>
<td>protonated m-Br species</td>
</tr>
<tr>
<td>MeOH</td>
<td>methanol</td>
</tr>
<tr>
<td>naphthyl</td>
<td>3-naphthyl-1,5-diphenylformazan</td>
</tr>
<tr>
<td>naphthyl(^-)</td>
<td>deprotonated naphthyl species</td>
</tr>
<tr>
<td>Symbol</td>
<td>Name</td>
</tr>
<tr>
<td>------------</td>
<td>-----------------------------------------------------------</td>
</tr>
<tr>
<td>naphthylH(^+)</td>
<td>protonated naphthyl species</td>
</tr>
<tr>
<td>o-Br</td>
<td>3-(2-bromophenyl)-1,5-diphenylformazan</td>
</tr>
<tr>
<td>o-Br(^-)</td>
<td>deprotonated o-Br species</td>
</tr>
<tr>
<td>o-BrH(^+)</td>
<td>protonated o-Br species</td>
</tr>
<tr>
<td>o-CH(_3)</td>
<td>3-(2-methylphenyl)-1,5-diphenylformazan</td>
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<td>deprotonated o-CH(_3) species</td>
</tr>
<tr>
<td>o-CH(_3)H(^+)</td>
<td>protonated o-CH(_3) species</td>
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<td>o-OH</td>
<td>3-(2-hydroxyphenyl)-1,5-diphenylformazan</td>
</tr>
<tr>
<td>o-OH(^-)</td>
<td>deprotonated o-OH species</td>
</tr>
<tr>
<td>o-OH(^+)</td>
<td>protonated o-OH species</td>
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<tr>
<td>OH-Cl</td>
<td>3-(2-hydroxy-4-chlorophenyl)-1,5-diphenylformazan</td>
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<td>deprotonated OH-Cl species</td>
</tr>
<tr>
<td>OH-ClH(^+)</td>
<td>protonated OH-Cl species</td>
</tr>
<tr>
<td>osc. str.</td>
<td>oscillator strength</td>
</tr>
<tr>
<td>p-CH(_3)</td>
<td>3-(4-methylphenyl)-1,5-diphenylformazan</td>
</tr>
<tr>
<td>p-CH(_3)(^-)</td>
<td>deprotonated p-CH(_3) species</td>
</tr>
<tr>
<td>p-CH(_3)H(^+)</td>
<td>protonated p-CH(_3) species</td>
</tr>
<tr>
<td>PFA</td>
<td>perfluoroacetic acid</td>
</tr>
<tr>
<td>TBAOH</td>
<td>tetrabutylammonium hydroxide</td>
</tr>
<tr>
<td>THF</td>
<td>tetrahydrofuran</td>
</tr>
<tr>
<td>TMAOH</td>
<td>tetramethylammonium hydroxide</td>
</tr>
<tr>
<td>TMF</td>
<td>trimethylformazan</td>
</tr>
<tr>
<td>TPF</td>
<td>triphenylformazan</td>
</tr>
<tr>
<td>UV</td>
<td>ultraviolet</td>
</tr>
</tbody>
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ABSTRACT

The spectroscopic characteristics of neutral, protonated and deprotonated triphenylformazans were investigated by means of visible absorption and $^1$H NMR spectroscopies. Studies of the effect of solvents and substituents on the absorption spectra of the neutral and ionic formazans were conducted. CNDO/S calculations for a series of formazans were performed to assign the electronic transitions observed in the absorption spectra of triphenylformazan.

The formazan system was found to be highly delocalized and not tautomeric as had been reported. The visible transition of the U (trans-syn) form of triphenylformazan was found to arise from orbitals localized on the formazan system. The near UV absorption of triphenylformazan has significant charge transfer character. The spectroscopic trends displayed by neutral and ionic triphenylformazans were found to be similar to those of the $\beta$-diketones.

The ionic forms of triphenylformazan derivatives were not photochromic. The anionic forms of the formazans were found to exist in equilibrium mixtures of U and S
(cis-syn) isomers that absorb at different wavelengths in the visible region. The equilibrium is affected by the nature of the solvent and by the presence of substituents on the carbon phenyl ring. The cationic forms of the derivatives were found to exist almost exclusively in the U geometry. The site of protonation is believed to be one of the nitrogen atoms which has phenyl substituents.
INTRODUCTION

Organization of This Dissertation

The research presented here was undertaken primarily to investigate the spectroscopy of protonated and deprotonated forms of triphenylformazan derivatives. This work is presented in six sections, namely: Introduction, Experimental, Absorption Spectra, NMR Spectra, Calculational Results and Discussion and Conclusions.

This Introduction contains a general discussion of the ideas which will be addressed in this dissertation. A discussion of the spectroscopy of triphenylformazan is given. No literature review will be presented; a recent, detailed literature review is given elsewhere.¹ The nomenclature used to describe the various geometrical forms of the triphenylformazans is introduced.

The Experimental section contains information on the instrumentation and chemicals used during the course of this research. A compendium of methods developed for the preparation of organic anions is also included. Few methods for the preparation of anions in solvents suitable for absorption spectroscopy had been developed
when this work was initiated.

The Absorption Spectra section contains the UV-visible absorption spectra of the neutral, deprotonated and protonated forms of the formazan derivatives that were studied. The interpretation of these spectra is, in general, presented in the Discussion and Conclusions section. The most important information taken from the absorption spectra is the wavelength of maximum absorption in the visible region of each form of the derivatives and the changes in the wavelength of maximum absorption in the visible region which accompany protonation, deprotonation and isomerization. Both types of information will be used in the Discussion and Conclusions section to determine the geometry of the protonated and deprotonated forms of the derivatives.

The section on NMR Spectra contains the $^1$H NMR spectrum of neutral, protonated and deprotonated triphenylformazan. The most important information taken from the NMR spectrum of neutral triphenylformazan is the number of phenyl proton peaks and the area under these peaks. This information is used to show that triphenylformazan contains a highly delocalized formazan system which exists in two different geometric isomers. The NMR spectra of ionic forms of triphenylformazan are
used to prove that the protonated and deprotonated forms of triphenylformazan were created. The NMR spectrum of deprotonated triphenylformazan in a solution that contains lithium ion is also presented. The number of phenyl proton peaks, the area under those peaks and the energy of the phenyl proton absorptions are used to show that the lithium containing derivative is similar to neutral triphenylformazan.

The Calculational Results section begins with a discussion of the CNDO method. The results of two sets of CNDO/S calculations pertaining to formazan derivatives are presented. These results will be used in conjunction with UV-visible spectra to determine the source of the absorption bands in the spectrum of triphenylformazan. Data from a set of CNDO/S calculations on cyclic azines are presented and discussed in terms of the ability of the CNDO method to treat carbon-nitrogen bonds successfully.

The Discussions and Conclusions section contains most of the interpretations of the absorption spectra of the formazan derivatives. Most of the conclusions in this work are based on general, often subtle, trends found in the absorption spectra. The conclusions are supported by calculational and NMR results.
Introduction to Formazan Chemistry

Triphenylformazan (TPF) is a naturally occurring, highly photochromic compound which has been investigated for many years.\(^1,2,3,4\) In solutions TPF exists in an equilibrium mixture of several geometric isomers of which at least two are chelated isomers and one is a nonchelated isomer.\(^1,2,4,5\) The chelated isomers predominate in solutions which have not been exposed to light.

Upon irradiation the hydrogen bond in the chelated forms is broken and isomerization occurs.\(^2,3\) The spectra of irradiated and nonirradiated DCM solutions of TPF are shown in Figure 1. The band in the 400 nm region of the irradiated solution spectrum arises from the absorption of nonchelated TPF.\(^1,4,5\) The irradiated solution is
FIGURE 1

Normalized Absorption Spectrum of TPF in ACN
a. —— non-irradiated solution
b. .... irradiated solution
yellow. The broad absorption band in the 485 - 525 nm region of the nonirradiated solution arises from the absorption of chelated forms of TPF.\textsuperscript{1,2,4,5} The nonirradiated solution is red.

The goal of the research presented in this dissertation was to investigate the protonated and deprotonated forms of triphenylformazan derivatives. When this work was begun the spectroscopy of neutral TPF had been extensively investigated. Results obtained for ionic forms of TPF appeared to contradict some generally held beliefs concerning the nature of the formazan system in TPF. This apparent contradiction prompted a series of CNDO/S calculations designed to investigate the origin of the absorption bands of neutral TPF. These calculational results combined with data from UV-visible absorption and $^1$H NMR spectroscopies shed new light on the nature of TPF.

Previous investigations of TPF have been primarily concerned with its photochromic properties.\textsuperscript{2,4,5,6,7,8,9} In many works emphasis has been given to the importance of the hydrogen bond in the chelated form of TPF.\textsuperscript{4,5,6,7,9} When this investigation was begun it was generally believed that only a hydrogen bonded chelate would absorb in the 485 - 525 nm region.\textsuperscript{4,5,9}
Results which indicate that undue emphasis has been placed on the effect of the hydrogen bond in the electronic properties of TPF will be presented. The geometry of a TPF molecule will be shown to have far greater importance than the presence or absence of a hydrogen bond in determining the spectroscopic, hence electronic, properties of TPF. For that reason the terms chelated and unchelated, ordinarily used to denote the red and yellow forms of TPF, will not be used in this work. A system of nomenclature developed by researchers in this lab to describe the geometry of β-diketones will be used in this dissertation to describe the geometry of triphenylformazans.\textsuperscript{10,11}

The terms U, S and W are used to denote the geometries of the β-diketones. These designations arise from the similarity of certain geometries of β-diketones to letters of the alphabet. It should be noted that the presence of a phenyl ring on the formazan carbon prevents the formation of a W isomer of the formazan derivatives examined in this work.

The U and S isomers of TPF shown on the following page are planar, idealized geometries. Unless otherwise stated, in this work the term planar refers to the
formazan system only and not to the complete molecule that contains phenyl substituents. Thus, a molecule in

\[
\begin{align*}
\text{U Form} & \quad \text{W Form} & \quad \text{S Form} \\
& \quad & \\
& \quad & \\
& \quad & \\
\end{align*}
\]

which \( N_1, N_2, C_3, N_4 \) and \( N_5 \) are contained in a single plane will be called planar whether the dihedral angles between that plane and the planes of the phenyl rings are or are not zero. The term coplanar will be used to denote formazan molecules in which the dihedral angle between the formazan system and its substituents is zero. It is likely that the TPF forms termed \( U \) and \( S \) are only approximately planar at best. The work of Veas\(^1\) indicates that at least two \( U \) forms of TPF exist. One of those forms is less nearly planar than the other form.
In this work the U form of TPF will refer to all geometric isomers of TPF in which H6 may form hydrogen bonds with both N1 and N5. Unless it is important to differentiate between the two U forms no distinction will be made. Such distinctions are probably artificial at best; it is likely that there are many U forms of TPF that vary somewhat from planarity. Though the S form of TPF shown on the previous page is planar, the degree of planarity of the observed S forms is unknown.

IR and resonance Raman studies of TPF have been undertaken by several investigators. These investigators assumed that non-irradiated TPF exists in a single U geometry. The formazan system in TPF has been called tautomeric in these studies. The term tautomeric in this instance means that the formazan system in TPF contains distinct single and double bonds. According to these researchers A and B shown above are tautomeric pairs not resonance isomers. Veas' work indicated that
non-irradiated TPF exists in at least two geometric isomers but did not address the issue of whether the formazan system in TPF is delocalized or tautomeric in nature.

Evidence in the form of NMR spectra will be presented which confirms Veas' finding that the U form of TPF exists in identifiably different geometric isomers. Additionally, these data will show that the formazan system in these isomers is delocalized, i.e. that A and B are resonance isomers not tautomeric pairs. A re-evaluation of published resonance Raman data which supports this idea will also be presented.

Anions of TPF derivatives were formed by deprotonation and their absorption spectra in polar and nonpolar solvents will be shown. The nature of the solvent will be shown to have a profound influence on the geometry of the deprotonated derivatives. The absorption spectra of deprotonated derivatives will show that formazans can absorb in the 500 nm region in the absence of chelation. Spectroscopic evidence that indicates that U forms of the anions of the formazan derivatives are quite rigid will be presented.

The spectra of protonated TPF derivatives in polar
and nonpolar solvents will be presented. The placement of the proton on the formazan system will be inferred from changes in the photochromic and spectroscopic properties of the derivatives which occur upon protonation. It will be shown from these data that the acidic proton probably attaches to N1 or N5.

Several TPF derivatives formed by substitutions onto the C3 phenyl ring have been studied. These derivatives include:

3-(2-bromophenyl)-1,5-diphenylformazan (o-Br),
3-(3-bromophenyl)-1,5-diphenylformazan (m-Br),
3-(2-hydroxyphenyl)-1,5-diphenylformazan (o-OH),
3-(2-hydroxy-4-chlorophenyl)-1,5-diphenylformazan (OH-Cl),
3-(2-tolyl)-1,5-diphenylformazan (o-CH₃),
3-(4-tolyl)-1,5-diphenylformazan (p-CH₃).

Other derivatives were formed by the substitution of a naphthyl group for the phenyl on C3 and by linking two formazan systems with a biphenylene bridge attached to C3. These derivatives are:

3-(2-naphthyl)-1,5-diphenylformazan (naphthyl)
1,1',5,5'-tetraphenyl-3,3'-(p-biphenylene)-diformazan (Diform)

The structures of all derivatives investigated in this
work are presented in the Appendix.

The absorption spectra of the neutral, anionic and cationic forms of these derivatives will be presented. The derivatives will be divided into three groups to facilitate the examination of their spectra. Group One derivatives have electronic and photochromic properties essentially identical with those of TPF. Group One contains TPF and the naphthyl, \( o-\text{CH}_3 \), \( p-\text{CH}_3 \), and \( m-\text{Br} \) derivatives. Group Two is composed of the \( o-\text{Br} \), \( o-\text{OH} \) and \( \text{OH-Cl} \) derivatives. The spectroscopic properties of Group Two compounds are markedly different from those of Group One. It will be shown that most of the differences between the spectroscopic properties of Group One and Group Two derivatives arise from differences in the geometries of the two sets of derivatives.

The diform derivative is examined separately. The spectroscopy of the diform derivative is similar to that of TPF. The existence of long wavelength absorption bands in the spectra of the various forms of the diform derivative set that derivative apart from the other formazans investigated in this work. The spectroscopic characteristics of the diform derivative will be interpreted in terms of the interaction between the formazan systems and the biphenylene bridge.
CNDO/S calculations relating to a variety of formazan systems were done. Results of these calculations will be used to aid in the identification of the nature of the absorption bands of the U form of TPF. It will be shown that phenyl substituents on the formazan system cause relatively minor perturbations of the electronic transitions of formazan, and that the absorption in the visible region of TPF in the U form arises from a transition localized on the formazan system. The limitations of the CNDO/S, MM2 and MNDO methods when applied to systems containing hydrogen bonded rings will be discussed.

Research in this laboratory for several decades has focused on the effects of small geometric changes on the electronic spectroscopy of organic molecules. Seminal work in this area involved the interpretation of the spectra of biphenyl and biphenyl derivatives. Studies of those systems showed that the existence of rotamers was responsible for the lack of structure in the absorption and emission spectra of biphenyl. Detailed studies of β-diketones have shown that the spectroscopy of those system is best interpreted in terms of molecules that are in geometrically different forms that casual thought might not differentiate. For the β-diketones
it has been shown that the energy of the absorption bands
is ordinarily \( E_U < E_S < E_W \).\(^{10,11}\) It has been postulated
that the rules developed to explain the electronic
spectra of the \( \beta \)-diketones may be applied to other
systems.\(^{11}\) This postulate has not been tested.

In this work it will be shown that triphenylformazans
follow spectroscopic trends similar to those of the
\( \beta \)-diketones. This conclusion is a significant
contribution to the effort to develop a set of guidelines
for the interpretation of the spectra of flexible
molecules.
EXPERIMENTAL

Mallinckrodt reagent grade methylene chloride (DCM), acetonitrile (ACN), carbon tetrachloride (CCl₄) and ethanol (EtOH) were distilled over calcium chloride before they were used. Mallinckrodt HPLC grade dimethylsulfoxide (DMSO) was dried over molecular sieves for several days and then was vacuum distilled. Care was taken to assure that the temperature during distillation was less than 298 K in order to prevent the formation of sulfides. DMSO purified in this manner was odorless and transparent at wavelengths longer than 250 nm. Reagent grade methanol (Mallinckrodt) was distilled over magnesium.

On numerous occasions it was necessary to use bulk methylene chloride, methanol and ethanol. These reagents were distilled twice before being purified in the usual manner. The spectroscopic characteristics of the purified bulk solvents were identical to those of the purified reagent grade solvents.

Reagent grade trifluoroacetic acid was distilled before use. Spectroscopic grade trifluoroacetic acid (Aldrich) was used without purification. Sodium
methoxide, potassium methoxide and tetramethylammonium hydroxide (TMAOH) were Aldrich products (98%). Solutions of 1.0 M (Aldrich) and 25% (Alfa) tetrabutylammonium hydroxide (TBAOH) in methanol were used. An Alfa solution of 25% TMAOH in methanol was also used. Lithium diisopropylamide (LDA) suspended in hexane and in a 1.5 M solution in tetrahydrofuran:heptane (3:2) were used. Hydrogen chloride was generated by dripping concentrated sulfuric acid onto either reagent grade sodium chloride or calcium chloride. The HCl was then dried by passing it slowly over an acetone/dry ice bath. Lithium chloride was recrystallized from boiling water and dried at 393 K.

The o-CH$_3$, p-CH$_3$ and diform formazan derivatives were products of U.S. Biochemicals. The spectroscopic properties of these compounds were not affected by recrystallization from MeOH and hexane. All other derivatives were synthesized and purified by Dr. Jerry Lewis using a modification of standard procedures.

Deuterated solvents used for NMR work were DMSO (99.9%), and ACN(99.5%); both were Aldrich products.

Perhaps the most difficult problem with spectroscopic studies of organic anions is the preparation of the ions in a solvent suitable for spectroscopy. Tetrahydrofuran
(THF) is commonly used as a solvent for organic ions but THF absorbs strongly in the near UV and, consequently, is unsuitable for spectroscopic measurements at wavelengths shorter than 320 nm. TBAOH and TMAOH were used to prepare anions in DMSO and ACN for the absorption studies done in this work, but they, too, have poor spectroscopic properties in the near UV. The absorption in the UV found when these reagents were used was probably not due to either the tetrabutylammonium or tetramethylammonium cations but to trace amounts of unsaturated quaternary ammonium cations. The formation of these unsaturated cations when saturated cations are heated is a well known reaction. All attempts to purify TBAOH and TMAOH resulted in increased absorption in the near UV.

A Cary model 14 spectrophotometer was used for UV-Vis absorption measurements. Ordinarily 1 cm silica cells were used. $^1$H NMR spectra were obtained by means of an AC/WP 200 MHz Bruker spectrometer.

Solutions used for spectroscopic measurements were freshly prepared. The concentrations of these solutions were unknown. Molar absorptivities of the derivatives investigated in this work were determined previously. Saturated solutions were used for NMR measurements. The molar absorptivity of TPF derivatives is on the order of
It is necessary to prepare large volumes of solution in order to know the concentration of solutions for absorption work with a reasonable degree of error. The price of the solvents necessary to make large quantities of solution is prohibitive. Concentration studies of the formazan derivatives investigated in this work were done previously.

Various methods of preparing TPF and other organic anions were developed by the author and Cristian Franco. Some of these methods are mentioned in various places in Franco's dissertation. The following list of the methods developed in this laboratory for the preparation of organic anions in solvents suitable for UV-Vis spectroscopy is included in this dissertation as a service to other researchers in the field.

**Preparation of Anions in Nonpolar Solvents**

The addition of $n$-butyl lithium in hexane to concentrated solutions (at least 0.05 M) of neutral substrates in benzene, toluene or long chain hydrocarbon solvents yields solutions of anions at concentrations on the order of magnitude of $10^{-5}$ M.

Anions may be prepared in $\text{CCl}_4$ and $\text{CS}_2$ by the
addition of one drop (approximately 0.05 ml) of 25% TBAOH in MeOH to a 10 ml solution of substrate (10^-5 M) in the appropriate solvent. Addition of more TBAOH/MeOH solution results in a two phase system and extraction of the anion into the MeOH layer. When properly prepared these solutions show no evidence of excessive light scattering.

Anions may also be prepared in CCl₄ by the addition of one drop of DMSO saturated with sodium dimsyl, potassium dimsyl or lithium dimsyl to 10 ml of a 10^-5 M solution of substrate in CCl₄. The preparation of dimsyl solutions is discussed below. Solutions prepared in this manner occasionally separate into two phases if they are disturbed. When properly prepared these solutions show no evidence of excessive light scattering.

Potassium, sodium and lithium may be dissolved in hexane/t-amyl alcohol solutions to yield a solvent appropriate for forming anions. Lithium reacts quite vigorously with t-amyl alcohol.

The addition one drop of lithium diisopropylamide in tetrahydrofuran:hexane to 25 ml of a long chain hydrocarbon yields a solution which can be used for the preparation of anions. The chief drawback to this method is the presence of excess LDA which reacts with several
Timothy Fillingim developed a method for the extraction of anions from metal complexes. The addition of crown ethers to solutions of dipyrrromethene complexes resulted in the complexation of the metal by the crown ether.

Preparation of Anions in Polar Solvents

Anionic species may be prepared in DMSO and ACN solutions by the addition of a few drops of concentrated dimsyl solution to 10 ml of 10^{-5} M solution of the substrate in the appropriate solvent. Concentrated solutions of potassium dimsyl, sodium dimsyl and lithium dimsyl may be prepared by the addition of the appropriate metal hydride to DMSO. Care should be taken in the preparation of potassium dimsyl; potassium hydride reacts vigorously with DMSO. Sodium hydride and DMSO react more slowly and require contact for at least 30 minutes. Sodium dimsyl solutions turn yellow after a few hours. Lithium hydride will not react with DMSO unless heated to at least 300 K. Excessive temperatures or prolonged heating results in yellow solutions. Dimsyl solutions absorb strongly in the near UV.
Anions may also be formed in solutions of TMAOH in DMSO. Crystalline TMAOH which is stored in air absorbs CO$_2$ and loses its solubility in DMSO. Saturated solutions of TMAOH in DMSO may be prepared by the adding an excess of TMAOH to DMSO and allowing the mixture to stand for 24 hours. The solution must be stored under an inert gas. Saturated TMAOH/DMSO solutions are soluble in ACN and may be used to form ions in that solvent. Crystalline TMAOH is insoluble in ACN. Anionic species may be formed by the addition of 1.0 M TBAOH in MeOH to DMSO, ACN and DMF.

Some anionic species may be prepared in 1.0 M TBAOH in MeOH and in 25% TMAOH in MeOH. Dilution of 1.0 M TBAOH with MeOH results in re-protonation of many anions.

Saturated solutions of alkali methoxides in DMSO may be prepared by allowing DMSO to stand over an excess amount of methoxide. Saturated solutions of alkali methoxides in ACN may be formed in the same manner. Ordinarily it is necessary to have an excess of the methoxide in contact with any substrate - ACN solution in order to prevent re-protonation. This method does not work for many substrates because they adhere to the excess methoxide. Solutions of methoxides in both DMSO and ACN begin to decompose within a few hours.
Solutions of sodium and potassium $t$-butoxide/$t$-butyl alcohol are useful for the formation of some anions. These solutions may be prepared by dissolving small pieces of the appropriate metal in $t$-butyl alcohol. This method should not be used for the preparation of lithium $t$-butoxide; the reaction of lithium and $t$-butyl alcohol is extremely violent.
ABSORPTION SPECTRA

Absorption Spectra of Group One

The spectra of neutral, nonirradiated TPF in various solvents are given in Figure 2. The absorption spectrum of neutral TPF is characterized by a broad band in the 475 - 550 nm region, a narrower, more intense band at 300 - 310 nm and a pair of unresolved bands at 260 - 270 nm. The broad band in the visible region originates from the absorption of at least two U forms of TPF. The origin of the band at 300 nm had not been investigated prior to this work but has been attributed to an absorption by at least one phenyl ring which is red-shifted by the formazan system. The nature of these two absorption bands will be discussed later. The bands at 260 nm are probably toluene-type bands arising from the phenyl rings.

The spectra of irradiated and nonirradiated TPF in DCM are given in Figure 1. Irradiation causes TPF in U geometries to convert to S geometries. This change in geometry induces a 70 nm blue shift of the visible absorption band and a decrease in the intensity of the 300 nm absorption band. The visible absorption band of the S geometries of TPF is considerably narrower than
FIGURE 2

Normalized Absorption Spectra of TPF in

a. ACN solution
b. CCl₄ solution
c. DMSO solution
d. DCM solution
that of the U geometries. The narrowness of the visible absorption band of the irradiated TPF solutions suggests that either TPF exists in only one S geometry or that all S geometries of TPF are quite similar.

Except when dissolved in DMSO, TPF is photochromic in all of the solvents studied. A sample of DMSO was dried and repeatedly cooled until it partially crystallized then vacuum distilled. TPF was not photochromic in that sample of DMSO. The photochromic behavior of TPF is reportedly quite sensitive to trace impurities in the solvent. During the course of this work it was observed that trace amounts, less than $10^{-7}$ M, of weak acids and bases destroy the photochromicity of TPF in ACN and DCM. DMSO itself is a stronger base than TPF and, though the existence of a trace contaminant can not be ruled out, it is likely that a specific solvent interaction prevents the photochromic activity of TPF in DMSO.

The absorption spectra of solutions composed of TPF and TBAOH or TMAOH in DMSO, ACN and CCl$_4$ are given in Figure 3. Evidence from $^1$H NMR experiments will be given later that proves TPF was deprotonated by the base in the DMSO solution. Deprotonated triphenylformazan (TPF$^-$) was not photochromic in any of the solvents studied.
FIGURE 3

Normalized Absorption Spectra of Deprotonated TPF in

a. — ACN solution
b. ......... DMSO solution
c. ..... CCl₄ solution
Figure 3
The absorption envelope in the visible region of TPF$^-$ in the two polar solvents appears to be composed of only one band. The single band in the visible region suggests that TPF exists in only one geometry in these solvents. The wavelength of maximum absorption of TPF$^-$ in the visible region is shifted 30 to 40 nm to the red of the more intense band in the visible region of the spectrum of neutral TPF in these solvents. The molar absorptivity of TPF$^-$ is roughly three times that of TPF.

TPF$^-$ in CC$\textsubscript{14}$ has three absorption bands in the visible; two fairly strong bands occur in the 500 - 550 nm region along with a weak absorption near 410 nm. The two bands in the 500 nm region appear to be single, asymmetric band in the absorption spectrum. The wavelength of maximum absorption of the anion in the 500 - 550 nm region is red-shifted about 30 nm from that of the neutral in CC$\textsubscript{14}$.

It is tempting to suggest that the reason there are two distinct bands in the 500 - 550 nm region of the CC$\textsubscript{14}$ solution is that there is an equilibrium between TPF and TPF$^-$. However, the decrease in the intensity of the absorption at 300 nm in this spectrum relative to that of neutral TPF in CC$\textsubscript{14}$ suggests that there is either very little or no neutral TPF in the solution. The intense
absorption near 275 nm arises from the presence of minute amounts of unsaturated quaternary ammonium cations which are present in the TBAOH/MeOH solution used to deprotonate TPF. The molar absorptivity of neutral TPF in CCl₄ is about 16,500 M⁻¹ cm⁻¹ at 500 nm and 24,500 M⁻¹ cm⁻¹ at 300 nm.¹ If either of the absorptions in the visible region were due to neutral TPF there would be an intense absorption near 300 nm.

The absorption spectrum of TPF⁻ contains no band centered in the 300 nm region. The spectral features at 300 nm were found to be indicative of the degree of deprotonation of TPF. The spectra of basic solutions that have no absorption band in the 300 nm region were unaffected by the addition of more base. Addition of excess base to basic solutions which did have an absorption band at 300 nm always caused changes in the absorption spectrum of the solution. The absorption band at 300 nm is characteristic of the neutral species.

With one exception, the absorption spectra of TPF⁻ solutions were found to be dependent on the solvent but independent of both the geometry of TPF before deprotonation and the nature of the base. The exception was the formation of TPF⁻ in solutions that contained lithium. The addition of salts containing Na⁺, K⁺, Rb⁺,
Cs⁺, Be⁺², Mg⁺², Ca⁺², and Ce⁺³ to solutions of TPF⁻ had no effect on the spectrum of the anion.

Figure 4 contains the spectra of solutions which were prepared by the addition of LiCl dissolved in DMSO to solutions containing TPF⁻. The absorption spectrum of Li⁺TPF⁻ in DMSO is reminiscent of the spectrum of TPF in DMSO. The visible absorption band of Li⁺TPF⁻ is less intense and broader than that of TPF⁻ but slightly more intense and narrower than that of neutral TPF. The wavelength of maximum absorption in the visible region of Li⁺TPF⁻ in DMSO occurs 5 nm to the red of that of TPF⁻ and 45 nm to the red of that neutral TPF. Li⁺TPF⁻ has an absorption band at 285 nm; this band is absent in the absorption spectrum of TPF⁻ and may be analogous to the 300 nm absorption band of TPF.

The spectrum of the ACN solution looks like the sum of the spectra of TPF⁻ and Li⁺TPF⁻. The absorption near 520 nm coincides with the absorption of non-lithium containing solutions of TPF⁻ in ACN. This result for ACN solutions is not surprising since most lithium salts are insoluble in ACN. Preparation of Li⁺TPF⁻ in hydroxide containing ACN solutions is further complicated by the gelation of lithium hydroxide. Li⁺TPF⁻ in the solvents studied was not photochromic.
FIGURE 4

Normalized Absorption Spectra of Li$^+\text{TPF}^-$ in

a. ——— DMSO solution

b. ——— ACN solution
Figure 4

Absorbance

Wavelength in nm
The observation that the absorption spectrum of TPF is unaffected by the counter ion, with the exception of Li\(^+\), is startling. Franco, working with dipyrromethenes, found an 8 nm shift in the absorption maximum of deprotonated dipyrromethene\(^{16}\) upon changing the counter ion from K\(^+\) to Na\(^+\) to Li\(^+\). These shifts in the visible absorption spectrum were accompanied by changes in the \(^1H\) NMR spectra. Additionally, Franco and Fillingim\(^{17}\) found shifts in the visible absorption maximum upon the addition of transition metal ions to solutions of deprotonated dipyrromethenes. Similar shifts in the spectra of TPF\(^-\) were not found. Shifts in the visible absorption band of formazyl complexes are quite small.\(^{19,20,21,22,23}\)

The absorption spectra of solutions of TPF and perfluoroacetic acid (PFA) or HCl in ACN and CC\(_4\) are shown in Figure 5. \(^1H\) NMR data that indicate that TPF is protonated by PFA in ACN solutions will be given later. Protonated triphenylformazan (TPFH\(^+\)) in the solvents studied was not photochromic. The maximum absorbance in the visible region of TPFH\(^+\) in ACN is 34 nm to the red of that of neutral TPF and has a second absorption band another 30 nm further to the red. The contour of the visible absorption band of TPFH\(^+\) is similar to but slightly narrower than that of the neutral species. The
FIGURE 5

Normalized Absorption Spectra of TPFH⁺ in
a ——— ACN solution
b. ———— CCl₄ solution
Figure 5

Absorbance

Wavelength in nm
molar absorptivity of TPFH⁺ is roughly twice that of TPF.

The spectrum of TPFH⁺ in CCl₄ is quite different than those of both TPF in CCl₄ and TPF⁺ in ACN. In the visible region of the spectrum of TPFH⁺ in CCl₄ two well defined bands of nearly equal intensity appear at 528 nm and 560 nm, a 30 nm red shift from the maximum absorption of TPF in the visible region. These absorption bands are about 1.5 times as intense as those of neutral TPF. There is a third, unresolved band in the 490 nm region that appears as a slight shoulder on the 528 nm band. A pair of unresolved bands occur at 640 nm and 610 nm. These low energy bands are almost as intense as the visible absorption bands of neutral TPF.

There is no absorption band in the neighborhood of 300 nm in the spectrum of TPFH⁺ in either solvent. Spectral features in this area were found to be useful for monitoring the degree of protonation of TPF.

The fact that neutral TPF in both the U and S forms has an absorption band in the 295 - 310 nm region and neither TPFH⁺ nor TPF⁻ have absorption bands in that region strongly suggests that the 310 nm absorption is an intramolecular charge-transfer band. Calculational data which support this conclusion will be presented later.
Figures 6, 7 and 8 show the non-normalized absorption spectra of the various forms of TPF in ACN, CCl₄ and DMSO respectively. The changes in intensity of the absorption bands which accompany protonation and deprotonation are shown in the spectra. In each solvent the the molar absorptivity in the visible region decreases in the order TPF⁻ > TPFH⁺ > TPF. The lack of an absorption band in the 300 nm region in the spectra of the deprotonated and protonated forms of TPF is apparent.

The spectra of neutral, protonated and deprotonated m-Br in ACN are shown in Figure 9. The absorption spectrum of neutral, nonirradiated m-Br in the visible region is composed of at least two unresolved bands. The wavelength of maximum absorption of the stronger band is at 475 nm. The weaker band appears as a shoulder near 525 nm. The long, low energy tail which extends past 600 nm suggests there may be a third band around 550 nm. The wavelength of maximum absorption in the UV is 304 nm. The 240 - 270 nm region is highly congested: there are at least four absorption bands in this area. These bands are not distinguishable in the spectrum shown in Figure 9. Veas found that the spectral and photochromic properties of the neutral m-Br derivative were quite similar to those of TPF.
FIGURE 6

Non-normalized Absorption Spectra of ACN solutions of

- a. — non-irradiated TPF
- b. . . . . irradiated TPF
- c. - — TPF
- d. -------- Li^+TPF
- e. ——— TPFH^+

The concentration of solution b was different from that of the other solutions.
Figure 6
FIGURE 7

Non-normalized Absorption Spectra of CCl$_4$ solutions of

a. --- neutral TPF

b. ------ TPF$^-$

c. ... TPFH$^+$
FIGURE 8

Non-normalized Absorption Spectra of DMSO solutions of

a. neutral TPF
b. TPF$^-$
c. TPFH$^+$
Normalized Absorption Spectra of ACN Solutions of

a. —— non-irradiated m-Br
b. —— irradiated m-Br
c. —— m-Br⁻
d. •••• m-BrH⁺
Figure 9
The spectrum of neutral, irradiated \( m\text{-Br} \) in the visible region is composed of a peak at 404 nm and lower intensity absorptions from 450 nm through 550 nm. The absorption band at 404 nm arises from \( m\text{-Br} \) in an S geometry, thus, the U to S isomerization causes a 71 nm blue shift of the wavelength of maximum absorption in the visible region. The absorption in the 450 - 550 nm region originates from \( m\text{-Br} \) in U geometries. The U to S conversion of \( m\text{-Br} \) in ACN is incomplete. There is a somewhat broad transition at 296 nm which has a shoulder near 305 nm; this broadness may result from the fact that the U and S isomers absorb at slightly different wavelengths in the 300 nm region. This transition is lower in intensity than the transition at 404 nm. The most intense absorption band in the spectrum occurs at 250 nm and has a shoulder at 262 nm. These spectral features are similar to those found for irradiated TPF.

The spectrum of the deprotonated \( m\text{-Br}^- \) derivative in the visible region contains a single intense band at 515 nm. A second, much weaker, band occurs at 410 nm. The wavelength of maximum absorption of \( m\text{-Br}^- \) is red-shifted 40 nm from that of neutral \( m\text{-Br} \). The 410 nm absorption band of the anion is red-shifted 5 nm from the maximum absorbance of neutral S forms of \( m\text{-Br} \). The transition at 515 nm is about 2.5 times as intense as the
475 nm transition of neutral m-Br. The spectrum of m-Br\textsuperscript{−} is the same whether the neutral m-Br in the S or U geometry is deprotonated. The spectral features of the m-Br\textsuperscript{−} derivative are similar to those found for TPF\textsuperscript{−}.

The absorption spectrum in the visible region of the protonated m-Br derivative (m-BrH\textsuperscript{+}) contains a band at 513 nm with a shoulder near 545 nm. There may be a second shoulder at 470 nm. There is a very low intensity transition in the 600 - 650 nm region. The molar absorptivity of m-BrH\textsuperscript{+} in the visible region is about 1.5 times that of neutral m-Br.

Neither m-Br\textsuperscript{−} nor m-BrH\textsuperscript{+} have transitions equivalent to the 300 nm transition of neutral o-Br. Neither ionic form of m-Br was photochromic. The similarity of the spectral features of ionic forms of m-Br to those of ionic forms of TPF indicates that the presence of the bromine has very little effect on the properties of the m-Br derivative. The influence of the bromine substituent is primarily seen in the appearance of the weak absorption band at 410 nm in the spectrum of m-Br\textsuperscript{−}.

The spectra of the o-CH\textsubscript{3} derivative in ACN and CCl\textsubscript{4} are given in Figure 10. The contours of the absorption spectra of o-CH\textsubscript{3} in both solvents are similar in the
FIGURE 10

Normalized Absorption Spectra of o-CH$_3$ in
a. —— ACN solution
b. ——— CCl$_4$ solution
visible region. The wavelength of maximum absorption in the visible region is 490 nm for the ACN solution. There is a second absorption which appears as a shoulder at 540 nm. The maximum absorbance in the UV occurs at 300 nm. There is another absorption in the UV at 270 nm.

The maximum absorbance in the visible region of the CCl\textsubscript{4} spectrum occurs at 498 nm. There is a second absorption in this region at 550 nm. There are three absorptions in the UV, the strongest occurs at 303 nm. The two remaining absorptions appear as shoulders at 266 nm and 274 nm. The general contours of the absorption spectra of neutral o-CH\textsubscript{3} in both solvents are reminiscent of those of neutral TPF in the same solvents.

The spectra of the deprotonated o-CH\textsubscript{3} derivative (o-CH\textsubscript{3}^-) in ACN and CCl\textsubscript{4} are shown in Figure 11. The spectrum of the ACN solution has a strong absorption band in the visible region centered at 525 nm. Deprotonation causes a 35 nm red shift in the wavelength of maximum absorption. There is a weak absorption band near 400 nm. The absorption spectrum of o-CH\textsubscript{3}^- in ACN is similar to those of TPF^- and m-Br^-\. The spectrum of the CCl\textsubscript{4} solution clearly results from the presence of both neutral and deprotonated o-CH\textsubscript{3} in solution. Repeated attempts to form pure o-CH\textsubscript{3}^- in CCl\textsubscript{4} were unsuccessful.
FIGURE 11

Normalized Absorption Spectra of \( o\text{-CH}_3^- \) in

a. ——— ACN solution

b. ——— CCl\(_4\) solution
Figure 11
The spectra of the protonated o-CH$_3$ derivative in ACN and CC$\text{Cl}_4$ solutions are shown in Figure 12. The absorption envelope in the visible region of the spectrum of the ACN solution is composed of at least two overlapping bands. The maximum absorbance of this solution occurs at 522 nm. There is an inflection point on the high energy side of this band near 490 nm. The general shape of the absorption band suggests that there may be a third band at a wavelength longer than 522 nm though there is only a slight inflection point at 570 nm on the low energy side of the band. The long tail which extends to 700 nm suggests there may be one or more low intensity bands in the 600 - 650 nm area.

The absorption contour in the visible region of the spectrum of o-CH$_3$H$^+$ in CC$\text{Cl}_4$ is composed of at least 3 bands. The maximum absorbance occurs at 536 nm. There is a well defined shoulder at 570 nm and an inflection point at 500 nm. This inflection point may indicate the presence of some neutral o-CH$_3$ in the solution although the addition of more acid to the solution did not cause a change in the absorption spectrum. There is at least one low intensity absorption in the 650 nm area.

The spectra of o-CH$_3$H$^+$ in both solutions contain low intensity absorption bands near 350 nm. The spectrum of
FIGURE 12

Normalized Absorption Spectra of o-CH₃H⁺ in
a. —— ACN solution
b. ........ CCl₄ solution
Figure 12
the ACN solution of o-CH$_3^-$ contain a band of similar intensity in the same region. The possible origins of these spectral features will be discussed after the spectra of the p-CH$_3$ derivative are presented.

Figures 13 and 14 give the non-normalized spectra of the various forms of o-CH$_3$ in ACN and CCl$_4$. The changes in intensity which accompany protonation and deprotonation are shown in these figures. The molar absorptivity in the visible region decreases in the order o-CH$_3^-$ > o-CH$_3$H$^+$ > o-CH$_3$ in the spectra of ACN solutions. The same trend in molar absorptivity was found for the various forms of TPF. In contrast to the spectra of the ionic forms of TPF, residual absorptions in the 300 nm region in the spectra of the ionic forms of the o-CH$_3$ derivative in both ACN and CCl$_4$ solutions are apparent.

The spectra of neutral and protonated p-CH$_3$ in CCl$_4$ are given in Figure 15. The maximum absorbance in the visible region of the spectrum of neutral p-CH$_3$ occurs at 495 nm, 3 nm to the blue of that of o-CH$_3$. There is a second absorption in the visible which appears as a shoulder at 542 nm, 8 nm to the blue of that of o-CH$_3$. The maximum absorbance in the UV region of the spectrum occurs at 305 nm, 2 nm to the red of that of o-CH$_3$. There is at least one unresolved band in the UV near 275 nm.
FIGURE 13

Non-normalized Absorption Spectra of ACN solutions of

a.—— neutral o-CH₃
b.--------- o-CH₃⁻
c.······ o-CH₃H⁺
Figure 13
FIGURE 14

Non-normalized Absorption Spectra of CCl₄ solutions of

a. ______ neutral o-CH₃
b. ------ o-CH₃⁻
c. ····· o-CH₃H⁺
FIGURE 15

Normalized Absorption Spectra of CCl₄ Solutions of

a. —— neutral p-CH₃

b. ——- p-CH₃H⁺
Figure 15
The spectrum is quite similar to those of o-CH₃ and TPF.

The wavelength of maximum absorption in the spectrum of the protonated form of the p-CH₃ derivative (p-CH₃H⁺) is at 538 nm, 2 nm to the red of that of o-CH₃H⁺. There is a second absorption at 570 nm which appears as a shoulder on the main absorption band in the visible. There is at least one low intensity transition near 650 nm. The spectral features of p-CH₃H⁺ are similar to those of o-CH₃H⁺.

Again in the spectrum of p-CH₃H⁺ there is a low intensity absorptions near 350 nm. This absorption is found only in the spectra of p-CH₃H⁺, o-CH₃H⁺ and o-CH₃⁻. As stated earlier, all the derivatives studied in this work were synthesized in this lab except the o-CH₃, p-CH₃ and diform derivatives. It is possible that the absorption found at 350 nm arises from contaminants. This hypothesis is also suggested by the fact that the 250 - 280 nm areas of the spectra of neutral o-CH₃ and p-CH₃ contain unresolved absorption bands, and the fact that the absorption bands in the 300 nm area of these spectra are abnormally broad. These features are not found in the spectra of any other neutral, anionic or cationic derivative with the exception of the diform derivative.
Both the $o$-$CH_3$ and $p$-$CH_3$ derivatives were recrystallized from MeOH and hexane. The spectra before and after recrystallization were the same. This result suggests that the unusual bands in the spectra of $o$-$CH_3$ and $p$-$CH_3$ may arise from the derivatives themselves, not from impurities. However, the appearance of solid $o$-$CH_3$ and $p$-$CH_3$ is markedly different from the appearance of all the other formazan derivatives, including the purchased diform derivative. The tolyl containing derivatives in the solid state are in the form of granules which tend to stick together. Significantly, the solid samples both before and after recrystallization smell slightly of toluene. It is possible that either these derivatives decompose or that toluene is intimately associated with the tolyl derivatives.

Figure 16 shows the spectra of ACN and $CCl_4$ solutions of the naphthyl derivative. The visible portion of the spectrum of the nonirradiated ACN solution contains at least two bands. The absorbance maximum in the visible occurs at 490 nm; there is a shoulder near 535 nm. The near UV absorption curve has a maximum at 315 nm and a shoulder near 325. Veas found multiple bands in the UV portion of the spectrum of the naphthyl derivative in a variety of solvents.
FIGURE 16

Normalized Absorption Spectra of Naphthyl in

a. — non-irradiated ACN solution

b. ----------- irradiated ACN solution

c. · · · CCl₄ solution
Figure 16
Upon irradiation the wavelength of maximum absorption of the ACN solution shifts to 403 nm. The absorption in the 400 nm region arises from S geometries of the naphthyl derivative. There may be a shoulder on the long wavelength side of this absorption band. The general shape of the absorption curve in the UV suggests that this curve is composed of several absorption bands. There are definite inflection points in this curve at 305 nm and 280 nm. The maximum absorbance in the UV occurs at 251 nm. The spectral features of the irradiated naphthyl solution differ from those of irradiated TPF solutions in the lack of definition of the bands in the UV region.

There are two bands in the visible region of the spectrum of the CCl₄ solution of the naphthyl derivative. The maximum absorbance in the visible region occurs at 500 nm. There is a second absorption band near 550 nm which appears as a shoulder on the main absorption band. There are two higher energy absorptions bands in the UV at 315 nm and 330 nm. In general the absorption spectrum of the CCl₄ solution is similar to that of the nonirradiated ACN solution.

The spectra of the deprotonated naphthyl derivative (naphthyl⁻) in ACN and CCl₄ are given in Figure 17. The maximum absorbance of the ACN solution occurs at 520 nm,
FIGURE 17

Normalized Absorption Spectra of Naphthyl⁻ in

a. ______ ACN solution
b. _______ CCl₄ solution
34 nm to the red of that of neutral naphthyl in ACN. The molar absorptivity of naphthyl\(^-\) in the visible region is approximately twice that of neutral naphthyl. There is an absorption at 420 nm, 17 nm to the red of that of neutral naphthyl in S geometries. There is an unresolved absorption band at 330 nm but the strong 315 nm band in the absorption spectrum of the neutral derivative is absent from the spectrum of naphthyl\(^-\). Naphthyl\(^-\) formed from the deprotonation of the naphthyl derivative in S geometries has the same spectrum as naphthyl\(^-\) formed from the deprotonation of naphthyl in U geometries.

The maximum absorbance of the CCl\(_4\) solution of naphthyl\(^-\) occurs at 540 nm. The absorption envelope in the visible region is quite broad and is composed of several bands. The absorption bands centered at 540 nm and 525 nm arise from either naphthyl\(^-\) or a mixture of neutral naphthyl and naphthyl\(^-\). There is a fairly weak band at 440 nm. The contour of the absorption spectrum from 360 nm to 410 nm suggests there may be a low intensity absorption band in that region. There is a broad absorption at 330 nm, but again the band at 315 nm which appears in the spectrum of the neutral derivative is absent in the spectrum of the deprotonated derivative. The deprotonation of the naphthyl derivative in CCl\(_4\) may be incomplete; the lack of a band at 315 nm in this
spectrum indicates that at least a significant fraction of naphthyl was deprotonated in the CCl₄ solution.

Figure 18 shows the spectra of ACN and CCl₄ solutions of the protonated naphthyl (naphthylH⁺) derivative. The visible region of the ACN spectrum contains a main absorption band with a maximum absorbance at 512 nm and a shoulder centered at 548 nm. These spectral features are shifted 32 and 13 nm to the red of the equivalent features in the spectrum of the neutral derivative. The molar absorptivity in the visible region of naphthylH⁺ is roughly 2.5 times that of neutral naphthyl. The general shape of the absorption envelope is similar to that of TPFH⁺ in the same solvent. There is a weak absorption band in the 310 - 340 nm region but this band probably originates from the naphthyl substituent.

The absorption spectrum of naphthylH⁺ in CCl₄ is similar to that of TPFH⁺ in CCl₄. The absorbance maximum occurs at 525 nm, a shift of 25 nm to the red of that of the neutral derivative. There is a pronounced shoulder near 555 nm, red-shifted 5 nm from that of the neutral derivative. At least one weak absorption occurs in the 600 to 650 nm region. Again, weak absorption bands occur in the 350 to 310 nm region.
FIGURE 18

Normalized Absorption Spectra of NaphthylH⁺ in

a. ——— ACN solution

b. ------ CCl₄ solution
Figure 18

Absorbance vs. Wavelength in nm
The fact that the 315 nm band found in the spectrum of neutral naphthyl is absent in the spectra of the anionic derivatives indicates that band is similar to the 300 nm band in the spectrum of TPF. The fact that the band near 330 nm occurs only in the spectra of the naphthyl derivative indicates that this band arises from the presence of the naphthyl group on the formazan ring. The spectrum of naphthalene contains a band at 312 nm and a second, weaker, band near 320 nm.

The fact that this 330 nm band also occurs in the spectrum of the deprotonated and protonated derivatives indicates that the nature of this band is different than that of the band at 315 nm. Veas found several bands in the near UV in the spectrum of the neutral naphthyl derivative which she attributed to the naphthyl substituent. Certainly if the 330 nm band arose from an intramolecular charge-transfer transition the band would not occur in the spectra of both the neutral and ionic forms of the derivative.

The general spectroscopic properties of Group One are:
- In neutral, nonirradiated solutions two U geometries that have absorption bands from 475 nm to 550 nm predominate.
Neutral forms of Group One derivatives are photochromic; ionic forms are not photochromic.

- The band near 300 nm in the neutral derivatives disappears upon protonation or deprotonation of the derivatives. The disappearance of this band in the spectra of CH₃ containing derivatives is partially masked by the apparent presence of an impurity. Relatively large amounts of PFA must be added to CCl₄ solutions in order to protonated formazans; the intense absorption which extends to 300 nm in many of the spectra of the protonated derivatives arises from the absorption of PFA.

- The visible absorption bands of deprotonated derivatives dissolved in polar solvents are narrower and about twice as intense as those of the neutral derivatives. These bands occur approximately 30 nm to the red of the visible absorption bands of the neutral derivatives.

- The spectra of deprotonated derivatives dissolved in CCl₄ contain two absorption bands in the 475 - 550 nm region. The maximum absorbance in the visible region of the spectrum of the deprotonated derivatives occurs about 30 nm to the red of those of the neutral derivatives.

- The intensity of the absorption near 400 nm in the spectra of the deprotonated derivatives is solvent dependent. In general the intensity of the absorption near 400 nm is greater when the deprotonated derivatives
are dissolved in CCl$_4$. The absorption near 500 nm is always more intense than that near 400 nm in the spectra of the deprotonated derivatives.

- The spectra of the protonated derivatives contain bands in the visible region between 475 nm and 550 nm. The maximum absorbance in the visible region of the spectra of the protonated derivatives occurs approximately 30 nm to the red of those of the neutral derivatives in U geometries. The molar absorptivity in the visible region of the protonated derivatives is roughly twice that of the neutral derivatives.

- The spectra of protonated derivatives dissolved in CCl$_4$ have low intensity absorption bands in the 600 - 650 nm region. Extremely weak absorption bands in the same region are found in the spectra of protonated derivatives dissolved in ACN.

Absorption Spectra of the Group Two

The spectra of ACN, DMSO, CCl$_4$ and MeOH solutions of neutral o-OH are given in Figure 19. These spectra show the profound influence of the nature of the solvent on the geometry of o-OH. The S geometry predominates in solvents which are capable of hydrogen bonding with the hydroxide group in the o-OH derivative. Even when the formazan is dissolved in CCl$_4$ there is a significant
FIGURE 19

Normalized Absorption Spectra of o-OH in

a. —— ACN solution
b. ----- DMSO solution
c.  .  CCl₄ solution
d. —— MeOH solution
amount of o-OH in the S geometry. The S form of o-OH in MeOH absorbs at 404 nm, about 130 nm to the blue of the more intensely absorbing U form.

The o-OH derivative is not photochromic. Veas conducted studies of the effects of temperature and solvent on the U:S equilibrium of the o-OH derivative.\(^1\) Based on work with alcohols, Veas concluded that the S form predominates when the o-OH derivative is dissolved in increasingly more acidic solutions. Veas's analysis satisfactorily explained the behavior of o-OH in alcoholic solvents but does not adequately explain the U:S distributions of the o-OH derivative found in the solutions studied in this work.

If solvent acidity alone affected S:U equilibrium then the S:U ratio in the solvents studied should reflect the acidity of the solvents, MeOH > ACN > DMSO. The S:U ratio found in these spectra decreases in the order DMSO > MeOH > ACN. The determining factor is probably the strength of the hydrogen bond formed between the hydroxide group and the solvent.

The spectra of ACN, DMSO and CC\(_4\) solutions of the deprotonated o-OH derivative (o-OH\(^-\)) are shown in Figure 20. The absorption band near 550 nm is more intense than
FIGURE 20

Normalized Absorption Spectra of $\text{o-OH}^-$ in

a. $\dashline ACN$ solution

b. $\dashdot$ DMSO solution

c. $\cdots$ $\text{CCl}_4$ solution
Figure 20

Absorbance

Wavelength in nm

675 625 575 525 475 425 375 325 275
that near 400 nm in the spectra of o-OH\(^{-}\) in polar solvents. The wavelength of maximum absorption in the visible region of the spectrum of the ACN solution occurs 40 nm to the red of that of neutral o-OH. The wavelength of maximum absorption in the visible region of the spectrum of o-OH\(^{-}\) in DMSO occurs 135 nm to the red of that of neutral o-OH. In both the ACN and DMSO solutions of the deprotonated derivative there is very little absorption in the 400 nm region. The maximum absorbance of o-OH\(^{-}\) in CCl\(_4\) occurs at 466 nm. There are shoulders near 430 nm and 502 nm. The wavelength of maximum absorbance of o-OH\(^{-}\) in CCl\(_4\) occurs approximately 70 nm to the blue of that of neutral o-OH.

The spectra of ACN, MeOH and CCl\(_4\) solutions of the protonated o-OH derivative (o-OHH\(^{+}\)) are shown in Figure 21. The general contour of the spectra of o-OHH\(^{+}\) is reminiscent of that of TPFH\(^{+}\) in the same solvents. There are at least two absorption bands in the 500 - 550 nm region of these spectra. The wavelength of maximum absorbance of o-OHH\(^{+}\) in ACN occurs 25 nm to the red of that of neutral o-OH in the same solvent. The wavelength of maximum absorbance of o-OHH\(^{+}\) in CCl\(_4\) occurs 11 nm to the blue of that of neutral o-OH in CCl\(_4\). Protonation of o-OH in MeOH solutions causes a 101 nm red shift in the wavelength of maximum absorbance; the S geometries
Normalized Absorption Spectra of o-OHH⁺ in

a. ——— ACN solution

b. ------ CCl₄ solution

c. ···· MeOH solution
predominate when neutral \( o-OH \) is dissolved in MeOH.

The spectra of ACN and \( \text{CCl}_4 \) solutions of the \( OH-Cl \) derivative are given in Figure 22. The spectra are quite similar to those of the \( o-OH \) derivative. The absorption in the 475 - 525 nm region of both spectra is more intense than that in the 350 to 400 nm region. The ratio of the absorbance near 500 nm to that near 400 nm is higher in the spectrum of the ACN solution than it is in that of the \( \text{CCl}_4 \) solution. These spectral features indicate that the U forms of \( OH-Cl \) predominate in both solutions and that ratio of \( S:U \) forms is greater in the ACN solution. The absorption in the 400 nm area of spectra of the \( OH-Cl \) derivative in both solvents is slightly greater than that of the \( o-OH \) derivative in the same solvents.

The spectra of ACN and \( \text{CCl}_4 \) solutions of the deprotonated \( OH-Cl \) derivative (\( OH-Cl^- \)) are shown in Figure 23. The spectra follow the same trends found for \( o-OH^- \). The maximum absorbance of \( OH-Cl^- \) in ACN occurs 40 nm to the red of that of neutral \( OH-Cl \) in the same solvent. The wavelength of maximum absorption of \( OH-Cl^- \) in \( \text{CCl}_4 \) is blue-shifted 75 nm from that of neutral \( OH-Cl \) in \( \text{CCl}_4 \).
FIGURE 22

Normalized Absorption Spectra of OH-Cl in

a. ——— ACN solution

b. ——— CCl₄ solution
Figure 22
FIGURE 23

Normalized Absorption Spectra of OH-Cl⁻ in

a. ——— ACN solution

b. ——— CCl₄ solution
The spectra of ACN and CCl₄ solutions of the protonated OH-Cl derivative (OH-ClH⁺) are given in Figure 24. The shifts in the wavelength of maximum absorbance which accompany protonation of the OH-Cl derivative are similar to those found for the o-OH derivative. The wavelength of maximum absorption of OH-ClH⁺ in ACN occurs 22 nm to the red of that of neutral OH-Cl in the same solvent. The maximum absorbance of OH-ClH⁺ in CCl₄ occurs 7 nm to the blue of that of neutral OH-Cl in CCl₄. The general contours of these spectra are similar to those of protonated TPF.

The fact that the o-OH derivative and the OH-Cl derivative display the same spectroscopic features suggests that the electron donating ability of the hydroxide group does not play a vital role in determining the spectroscopic properties of these derivatives. In the OH-Cl derivative the chlorine atom, which is a moderately strong electron withdrawing group, is in the para position with respect to the hydroxy group. The net electron donating strength of the substituted phenyl in the OH-Cl derivative is probably similar to that of the tolyl ring in the o-CH₃ derivative but the spectroscopy of these derivatives is quite different.

The primary chemical difference between the o-CH₃
FIGURE 24

Normalized Absorption Spectra of OH-ClH⁺ in

a. ---- ACN solution

b. ------- CCl₄ solution
derivative and the OH-Cl derivative is the ability of the hydroxy moiety of the OH-Cl derivative to hydrogen bond to either the formazan system or to a solvent molecule. Hydrogen bonding between the methyl group of the o-CH$_3$ derivative and the formazan system or a solvent molecule is extremely unlikely.

The spectra of ACN and CC$_4$ solutions of the o-Br derivative are shown in Figure 25. Like the o-OH and OH-Cl derivatives, the o-Br derivative is not photochromic. The visible region of the absorption spectrum of o-Br in ACN contains a single band at 404 nm; the S geometries of o-Br predominate in ACN solutions. The spectrum of o-Br in ACN is reminiscent of that of the S form of TPF in DCM. The visible region of the absorption spectrum of o-Br in CC$_4$ contains a series of bands with decreasing intensity at 415 nm, 435 nm, 470 nm and 530 nm. The S geometries of o-Br predominate in CC$_4$ solution but there is a significant amount of o-Br in U geometries.

The spectra of ACN and CC$_4$ solutions of the deprotonated o-Br derivative (o-Br$^-$) are given in Figure 26. The wavelength of maximum absorbance of o-Br in ACN is red-shifted 112 nm from that of the neutral o-Br in the same solvent. The maximum absorbance of o-Br$^-$ in CC$_4$
FIGURE 25

Normalized Absorption Spectra of o-Br in

a.—— ACN solution

b.------- CCl₄ solution
Figure 25
Normalized Absorption Spectra of o-Br⁻ in

a. ——— ACN solution

b. ------- CCl₄ solution
occurs approximately 100 nm to the red of that of neutral o-Br in CCl₄. The spectra of o-Br⁻ in both solvents are similar to the spectra of TPF⁻. The shifts in wavelength of maximum absorbance are of the same order of magnitude of those associated with the deprotonation of TPF in S geometries.

The spectra of ACN and CCl₄ solutions of the protonated o-Br derivative (o-BrH⁺) are shown in Figure 27. The general shape of the visible absorption bands in these spectra are reminiscent of those of o-OHH⁺ and TPFH⁺ in the same solvents. The wavelength of maximum absorption of o-BrH⁺ in ACN is red-shifted about 110 nm from that of neutral o-Br in ACN. The absorbance maximum of o-BrH⁺ in CCl₄ is red-shifted about 100 nm from that of neutral o-Br in CCl₄. These shifts are of the same order of magnitude as those found for the protonation of S forms of the naphthyl derivative.

In some respects the o-Br derivative doesn't fit into the same group as the o-OH and OH-Cl derivatives. The bromine substituent is obviously not capable of hydrogen bonding with the formazan system. However, the bromine can hydrogen bond to protic solvents. Veas' work showed that the spectroscopy of the o-Br derivative is substantially affected by the nature of the solvent. In
FIGURE 27

Normalized Absorption Spectra of o-BrH⁺ in

a. ——— ACN solution

b. ———— CCl₄ solution
Figure 27
protic solvents the S isomer predominates. It is reasonable to expect an interaction between the bromine substituent and the slightly acidic protons on ACN. The clustering of ACN molecules about the bromine would create a steric strain that would destabilize the U form of the neutral derivative.

The general spectroscopic properties of Group Two are:

- None of the neutral derivatives is photochromic. There is an equilibrium mixture of U and S forms of each derivative in solution. The equilibrium increasingly favors the S form as a derivative is dissolved in increasingly more polar solvents.

- The deprotonated derivatives are not photochromic. There is significant absorption in both the 400 nm and 525 nm regions of the spectra of the deprotonated derivatives. The ratio of the intensity of the absorption bands in the 525 nm area to that in the 400 nm area increases as the deprotonated derivatives are dissolved in increasingly more polar solvents.

- The magnitude and direction of the shifts in the wavelength of maximum absorbance in the visible region which accompany deprotonation vary tremendously from derivative to derivative and are solvent dependent.

- The protonated derivatives are not photochromic.
The absorption spectra of the protonated derivatives, which are similar to that of protonated TPF, generally have two overlapping bands in the 475 - 550 nm region. The magnitude of the shifts in the wavelength of maximum absorbance in the visible region caused by protonation vary widely among the derivatives and are solvent dependent.

- The 300 nm region of the spectrum is not a good indicator of the ionic state of the derivative. This difference from the TPF group arises from the fact that when the S isomer predominates in the neutral form the absorption in the 300 nm region is much weaker than the absorption in that region when the U isomer predominates.

Absorption Spectra of the Diform Derivative

The spectra of ACN, DMSO, MeOH and CCl₄ solutions of the diform derivative are given in Figure 28. With the exception of the spectrum of the MeOH solution, all the spectra are normalized to an absorbance of 1.00 in the visible region. The spectrum of the MeOH solution is normalized to 0.50 in the visible region; the absorption near 300 nm in the MeOH solution is extremely intense. The spectra of the diform derivative are similar to those of TPF. The primary difference arises from the increased absorption at long wavelength in the visible region of
FIGURE 28

Normalized Absorption Spectra of Diform in

a. ——— ACN solution
b. --------- DMSO solution
c. .... MeOH solution
d. ——— CCl₄ solution
the spectra of the diform derivative. The wavelength of maximum absorbance in the visible region varies from 560 nm in the DMSO spectrum to 495 nm in the MeOH spectrum. The only spectrum which contains more than one well defined band in the visible region is that of the MeOH solution. The spectrum of the diform derivative in other solvents contain many overlapping absorption bands which form a very broad, featureless absorption envelope in the visible region. The U form predominates in each solution although presence of the S form is apparent from the absorption in the 400 nm region of the spectra.

The diform derivative is composed of two formazan systems linked by a biphenylene bridge via the carbon atoms in the formazans. The geometry of each formazan system in a single molecule may be different. Lewis and Sandorfy\textsuperscript{6} studied the photochromicity of a similar derivative, a diformazan linked by a biphenylene bridge that connected the nitrogen atoms in the formazan systems. Their work shows that all of the bands in the absorption spectra of both irradiated and nonirradiated diformazan solutions may be attributed to normal absorptions of U and S TPF. No band in the spectra was attributed to the absorption of the entire molecule acting as a unit.
The normal TPF absorption band found near 300 nm occurs in the spectra of the diform derivative. This band is somewhat broadened in the spectra of diform. The molar absorptivity at the 300 nm of diform in MeOH is about twice the molar absorptivity in this region of diform in the other solvents studied. The intensity of 300 nm band in the spectra of all other derivatives is fairly insensitive to solvent.

The spectra of ACN, DMSO and CCl₄ solutions of the diform derivative (diform⁻) are shown in Figure 29. In the spectra of the ACN solutions the maximum absorbance in the visible region shifts from 520 nm for the neutral derivative to 590 nm for the anion. There is a well defined shoulder in the visible region absorption near 510 nm. The absorption in the spectrum of the neutral form at 302 nm is absent in the spectrum of the anion. A weak absorption band occurs in the 400 nm region.

In the spectra of the DMSO solutions the maximum absorbance in the visible region shifts from 560 nm for the neutral derivative to 610 nm for the anion. There is a clear shoulder in the visible region absorption near 525 nm and noticeable absorption in the 400 nm region. The weak absorption at 320 nm is not affected by the addition of excess base.
FIGURE 29

Normalized Absorption Spectra of Diform$^-$ in

a. — ACN solution
b. ——— DMSO solution
c. · · · · CCl$_4$ solution
In the spectra of the CCl₄ solutions the maximum absorbance in the visible region shifts from 555 nm for the neutral derivative to 615 nm for the anion. There is a shoulder in the visible region absorption curve near 520 nm. There is a significant absorption at 405 nm. There is no absorption band in the 300 nm region.

The spectra of diform⁻ are much broader than the spectra of TPF⁻ in the same solvents. Deprotonation induces a red-shift in the visible absorbance maximum of both TPF and diform solutions but the magnitude of the shift is much greater in diform solutions (50 - 70 nm) than in TPF solutions (30 - 35 nm). The absorption maximum occurs near 525 nm in the spectra of TPF⁻; the wavelength of maximum absorption of diform⁻ solutions occurs from 590 to 615 nm. There is a distinct shoulder near 525 nm in the spectra of diform⁻ in CCl₄ and DMSO solutions. There may be an inflection point in the spectrum of the ACN solution of diform⁻, certainly the broadness and asymmetry of the visible absorption envelope suggest the existence of an underlying absorption in the 500 - 550 nm region.

The spectrum of a DMSO solution of diform⁻ and lithium chloride is shown in Figure 30. The absorbance maximum occurs at 620 nm, 10 nm to the red of that of the
Absorption Spectrum of Li$^+$Diform$^-$ in DMSO
diform\textsuperscript{−} solution which does not contain lithium and 60 nm to the red of the maximum absorbance of neutral diform. The general shape of the absorption contour is similar to that of the neutral derivative. The absorption band at 320 nm is present in the spectrum of the solution that contains lithium although it is less intense than the same band in the spectrum of the neutral derivative. These results are similar to those found for TPF\textsuperscript{−} in solutions that contain lithium.

The spectra of ACN and CCl\textsubscript{4} solutions of the protonated diform derivative (diformH\textsuperscript{+}) are given in Figure 31. These spectra were obtained from solutions with very high concentrations of PFA; both spectra contain extremely intense bands which extend from the 325 nm region to 225 nm that originate with PFA. The ACN solution of diformH\textsuperscript{+} has a maximum absorbance in the visible region at 540 nm, 20 nm to the red of that of the neutral derivative. There is a low intensity, long wavelength tail which extends to 735 nm. The strong absorption band in the spectrum of the neutral derivative at 302 nm is absent from the spectrum of the cation.

The absorption of the protonated form in CCl\textsubscript{4} in the visible region is extremely broad, extending into the near infrared region. The maximum absorbance occurs at
FIGURE 31

Normalized Absorption Spectra of DiformH$^+$ in
a. $\cdots$ ACN solution
b. $\cdots$ CCl$_4$ solution
605 nm, 50 nm to the red of that of the neutral derivative. There is second, somewhat defined, absorption band near 560 nm. No absorption band occurs in the 310 nm area which indicates that the 560 nm absorption does not arise from trace amounts of the neutral derivative.

The spectroscopic properties of the diform derivative are similar to those of TPF. The major difference is the broadness of the absorptions in the diform spectra. The broadening in the spectra of all three forms of the diform derivative occurs on the long wavelength side of the visible absorption bands. The forces which give rise to this broadening will be discussed later.

Summary

The division of the formazan derivatives examined in this work into three groups is, in many ways, artificial, but it is a useful division for a discussion of the spectroscopy of the individual derivatives. An overview of the spectroscopic trends is important for the understanding of the details of the spectra of many derivatives.

The spectroscopic trends found for triphenylformazan derivatives are:
- The photochromism of formazan derivatives is affected by both solvent and substituent. No derivative is photochromic when it is dissolved in DMSO. Derivatives that have substituents in the ortho position that may strongly interact with either the formazan system or the solvent are not photochromic.

- The U:S equilibrium is solvent dependent for all neutral derivatives. The influence of solvent on this equilibrium is more pronounced in derivatives that have substituents in the ortho position that may interact strongly with the solvent.

- The S forms of neutral derivatives have absorptions approximately 70 nm to the blue of U forms. The S form of some derivatives, such as TPF and other Group One derivatives, are created by irradiation of U forms. The S form of other derivatives, such as o-OH and other Group Two derivatives, are formed by dissolving the derivative in a solvent which stabilizes the S form. All neutral S forms absorb near 400 nm, approximately 70 nm to the blue of the U forms of those derivatives.

- The visible absorption bands in the spectra of all forms of the diform derivative are significantly broader than those in the spectra of the same forms of all other derivatives. No substituent other than biphenylene significantly affects the breadth of the visible absorption bands.
- No ionic form of any derivative was photochromic in any of the solvent systems that were studied.

- The protonated forms of all derivatives have some absorption in the 600 - 650 nm region. Many derivatives display only trace absorption in this area. The intensity of the absorption near 625 nm is dependent on both solvent and substituent. For all derivatives, the intensity of absorption in this region is most intense when CC\textsubscript{4} is the solvent. The long wavelength absorption is most pronounced in the spectrum of the diform derivative.

- The spectra of protonated forms of all derivatives have two overlapping bands in the 475 - 550 nm region. The spectrum of the protonated diform derivative appears to be composed of at least three overlapping bands due to the intensity of the long wavelength band. The 475 - 550 nm bands occur 30 - 40 nm to the red of the more intense absorption bands of the neutral U forms. In cases in which a direct comparison is possible the visible absorption band of protonated forms is about twice as intense as that of neutral U forms dissolved in the same solvent.

- All protonated forms have less absorption in the 400 nm region of the spectrum than neutral and deprotonated forms of the derivatives. Neutral S forms absorb in this region.
- The wavelength, width and intensity of visible absorptions of deprotonated derivatives are strongly influenced by the nature of the solvent and substituents. All deprotonated derivatives have some absorption in both the 525 nm and 400 nm regions.

- Deprotonated derivatives that do not contain ortho positioned substituents that may strongly interact with the formazan system or the solvent always absorb more strongly near 525 nm than near 400 nm.

- The absorption of deprotonated forms in the 400 nm region increases as the derivatives are dissolved in increasingly less polar solvents. Each deprotonated derivative absorbs most strongly in the 400 nm region when it is dissolved in CCl₄.

- The effect of the nature of the solvent on the wavelength of the visible absorption bands of deprotonated derivatives is much more pronounced for derivatives that have substituents in the ortho position that can interact with the solvent or the formazan system. The 400 nm absorption is more intense than that near 525 nm when these deprotonated derivatives are dissolved in CCl₄. Neutral S forms absorb near 400 nm.

- Deprotonated derivatives dissolved in polar solvents have a single absorption band near 525 nm. In cases in which direct comparisons can be made the 525 nm region absorption of the deprotonated derivatives is
narrower and about twice as intense as that of the neutral U forms. The absorption band of deprotonated forms near 525 nm occurs, in general, approximately 30 - 40 nm to the red of that of neutral U forms.

- Deprotonated derivatives dissolved in CCl₄ have multiple absorption bands in the visible region. The deprotonated derivatives that have more intense absorptions near 525 nm when dissolved in CCl₄ have two overlapping bands in that region. The visible absorptions of these deprotonated derivatives are about twice as intense as the those of the neutral derivatives in CCl₄. Deprotonated derivatives that have more intense absorptions near 400 nm have two to four overlapping absorptions in that region.

- The only counter ion which affects the absorption spectrum of deprotonated derivatives is Li⁺. The visible absorptions of deprotonated derivatives in the presence of lithium are red-shifted from those of deprotonated derivatives not associated with lithium. While the absorption bands of solutions of deprotonated derivatives containing lithium are more intense and occur at longer wavelengths than those of the neutral derivatives, the spectra of deprotonated derivatives associated with lithium resemble those of U forms of the neutral derivatives.
The proton NMR spectrum of TPF had been studied prior to this work.\textsuperscript{1,24} Veas, studying the rate of exchange of the formazan and hydroxy protons in the o-OH derivative with the deuterium atoms in the solvent molecules, noted that the apparent resolution of the phenyl peaks was affected by the solvent. Veas obtained proton NMR spectra by means of a 100 MHz spectrometer; cyclohexane and acetonitrile were the solvents. The reported spectra contain four unresolved sets of peaks in the region where phenyl protons absorb, 7 to 8 ppm. Absorptions by the phenyl protons appeared to be slightly better resolved when cyclohexane was the solvent.

The 200 MHz proton NMR spectrum of a DMSO solution of TPF is shown in Figure 32. The peak at 14.2 ppm arises from the absorption of the formazan proton; the phenyl protons absorb in the 7 to 8 ppm area. Triphenylformazan contains one formazan proton and 15 phenyl ring protons, therefore, the ratio of the area under the phenyl peaks to that under the formazan peak should be 15:1. The expected ratio was found for this and all other $^1$H NMR spectra recorded from fresh solutions.
FIGURE 32

$^{1}H$ NMR Spectrum of TPF in DMSO
In the absence of complications due to geometry, the 200 MHz proton spectrum of a single phenyl ring attached to the formazan system should be a quartet. It is unlikely that a phenyl ring attached to the carbon in the formazan system would be equivalent to those attached to the nitrogens, therefore, the proton NMR spectrum of TPF should contain two quartets of phenyl proton peaks. One quartet should correspond to the protons on the phenyl rings attached to the two nitrogens; the other quartet should arise from protons on the carbon phenyl ring. The ratio of the area of the nitrogen phenyl peaks to that of the carbon phenyl peaks should be 2:1. The distribution of the area under the formazan, carbon phenyl and nitrogen phenyl peaks should be 1:5:10.

These arguments are based on the assumption that the geometry of the formazan system will not affect the NMR spectrum. That is probably not a good assumption. The geometry of the formazan system affects the formazan π cloud that, in turn, affects the phenyl π clouds. Any change in the electronic field near the phenyl protons will cause a change in the energy required to flip those protons.

TPF in solution is known to exist in at least two geometries. Each geometric form of TPF will give an NMR
signal if the rate of conversion between the two geometric forms is slow on the NMR time scale. If TPFA and TPFB represent the two geometric forms then the NMR spectrum of a TPF solution should be the sum of the spectra of TPFA and TPFB. The phenyl protons on TPFA should give rise to two quartets. The ratio of the area under the two quartets should be 1:2 corresponding to the area of the carbon phenyl protons and nitrogen phenyl protons. The same pattern should be obtained for TPFB. Therefore, the phenyl portion of the spectrum of TPF should be composed of four quartets, two quartets for each geometric form. The distribution of the normalized area under the quartets should be A:2A:B:2B. The ratio of TPFA to TPFB in solution would then be A:B.

The phenyl portion of the 200 MHz proton NMR spectra of saturated DMSO and ACN solutions of TPF are shown in Figures 33 and 34 respectively. These spectra contain four sets of peaks. If the area under the formazan proton peaks, not shown in these figures, is normalized to 1.0 then the total area under all the phenyl peaks equals 15 for both the ACN and DMSO spectra. The ratio of the area under the peaks near 8.1 ppm to those near 7.8 ppm is 1.36:2.71 or 1:2.01 in the ACN spectrum; the ratio is 9.42:20.2 or 1:2.14 in the DMSO spectrum. The ratio of the area under the quartet near 7.35 ppm to that near
FIGURE 33

Phenyl Portion of the $^1$H NMR Spectrum of TPF in DMSO
FIGURE 34

Phenyl Portion of the $^1$H NMR Spectrum of TPF in ACN
7.5 ppm is 2.16:4.31 or 1:2.00 for the ACN spectrum; the ratio is 17.9:35.4 or 1:1.98 in the DMSO spectrum. These spectra have area distributions of A:2A:B:2B.

The high field, low ppm, peaks occur at approximately the same energy in both spectra. There are two sets of quartets in the DMSO spectrum between 7.3 and 7.6 ppm. These same quartets, with additional splittings, are found in the ACN spectrum. The major peaks in the ACN spectrum occur within ±0.01 ppm of those in the DMSO spectrum. Table 1 contains a listing of the peaks found in both spectra.

The low field, high ppm, peaks in the ACN spectrum are shifted slightly from those in the DMSO spectrum. The peaks that occur near 7.8 ppm in the ACN spectrum are shifted 0.07 ppm downfield from the equivalent peaks in the DMSO spectrum. The peaks near 8.1 ppm in the ACN spectrum are 0.12 ppm upfield from the equivalent peaks in the DMSO spectrum.

These spectra demonstrate the effect found by Veas. The phenyl peaks in spectrum of the ACN solution, similar in shape to those of the DMSO solution spectrum, appear better resolved than those of the DMSO spectrum. At first glance it appears that the high number of splittings
found in the ACN spectrum may result from poor shim settings on the NMR spectrometer. However, close examination of the DMSO spectrum reveals that the peaks in that spectrum are asymmetric. The shoulders in the DMSO spectrum peaks are consistent with the multiple splittings found in the ACN spectrum. This phenomenon is particular clear in the peaks at 8.01, 7.37 and 7.34 ppm in the DMSO spectrum. The peak at 8.01 ppm has a shoulder on the high ppm side, consistent with the split peak found at 8.13 in the ACN spectrum. The peak at 7.37 ppm in the DMSO spectrum is asymmetric and is obviously split; the 7.37 ppm peak in the ACN solution is split into a triplet. Additionally, in each ACN solution spectrum recorded the internal reference, tetramethylsilane, gives a single, symmetric peak at 0.0 ppm. Evidently, the splittings found in the ACN solution spectrum arise from TPF, not from poor shim settings in the spectrometer.

The proton NMR spectrum of a DMSO solution of TPF and TBAOH is shown in Figure 35. The dramatic difference in the general shapes of this spectrum and that of neutral TPF in DMSO is proof that TPF is deprotonated by TBAOH. The overall upfield shift of the phenyl proton peaks in this spectrum relative to those in the spectrum of neutral TPF in DMSO indicates that the electron density
FIGURE 35

$^{1}\text{H NMR Spectrum of Deprotonated TPF}$
on the phenyl rings is significantly higher in TPF⁻. Attempts to record the ¹H NMR spectrum of TPF⁻ in ACN were unsuccessful; TPF⁻ is not soluble enough in ACN to prepare a solution of the concentration necessary to perform NMR experiments.

The proton NMR spectrum of a DMSO solution of deprotonated TPF and lithium chloride is shown in Figure 36. A comparison of this spectrum with that of deprotonated TPF shows that the presence of the lithium cation has a profound effect on TPF⁻. The spectra do not resemble one another. A comparison of the Li⁺TPF⁻ spectrum with that of neutral TPF in DMSO shows that the Li⁺TPF⁻ spectrum is quite similar to that of TPF. Both spectra contain four distinct groupings of absorption peaks. There are structureless peaks at 8.0 ppm and 7.8 ppm in the spectrum of the lithium solution which correspond to peaks at 8.0 ppm and 7.8 ppm in the spectrum of neutral TPF. The somewhat structured upfield peaks centered at 7.3 ppm and 7.1 ppm in the lithium spectrum are equivalent to those centered at 7.5 ppm and 7.35 ppm in the spectrum of neutral TPF. The ratio of the area under the two downfield peaks is 1:2.02 in the lithium spectrum and 1:2.14 in the spectrum of neutral TPF. The ratio of the area under the two upfield peaks is 1:1.99 for the lithium spectrum; the ratio of the area
FIGURE 36

$^{1}H$ NMR Spectrum of Li$^{+}$TPF$^{-}$
under the equivalent peaks in the spectrum of neutral TPF is 1:1.98. The lithium spectrum, like that of neutral TPF, has an area distribution of A:2A:B:2B.

In the spectrum of neutral TPF in DMSO the two downfield peaks at 8.0 and 7.8 ppm are split into doublets. The separation between the peaks comprising the doublet at 8.0 is 0.035 ppm; the separation between those of the doublet at 7.8 ppm is 0.040 ppm. These doublets appear to be single, broad, unstructured peaks in the spectrum of the solution in which there is lithium ion. The peak centered near 7.5 ppm in the spectrum of neutral TPF is split into a well defined quartet. The equivalent peak in the lithium spectrum is centered near 7.3 ppm and is split into a somewhat unresolved quartet. The separation between the two most intense peaks in the quartet near 7.5 in the spectrum of neutral TPF is 0.040 ppm; the splitting between the two most intense peaks in the equivalent quartet in the lithium containing spectrum is 0.040 ppm. There is a quartet in the spectrum of neutral TPF near 7.3 ppm which is equivalent to an asymmetric triplet located near 7.1 ppm in the spectrum of the lithium containing solution. The separation between the two most intense peaks in the quartet in the neutral TPF spectrum is 0.036 ppm; in the lithium spectrum the splitting between the peaks in the triplet
is 0.036 ppm.

The spectrum of Li\(^+\)TPF\(^-\) was that of a viscous solution. All solutions which contain both lithium cations and hydroxide at the concentrations necessary for NMR experiments are highly viscous. In general as the viscosity of a solution increases the apparent resolution of NMR spectra decreases due to an increase in the longitudinal relaxation time. The bandwidth of an NMR peak is determined by the longitudinal and latitudinal relaxation times. As the longitudinal relaxation time of a proton increases the bandwidth of the absorption peak associated with that proton also increases.

The comparison of the spectrum of Li\(^+\)TPF\(^-\) with that of neutral TPF showed that the line broadening that occurs in the spectrum of the lithium solution was not uniform. The apparent loss of resolution in the two downfield sets of proton absorptions is much greater than that of the two upfield sets of proton absorptions. For the downfield absorptions, peaks separated by 0.040 ppm in the spectrum of the neutral solution appear as a single, broad hump in the spectrum of the lithium solution. For the upfield absorptions, peaks separated by 0.040 ppm in the spectrum of the neutral solution appear as broadened but distinguishably separate peaks in the
spectrum of the lithium solution. The fact that the line broadening found for the two upfield absorptions is different from that of the downfield absorptions strongly suggests that the upfield absorptions arise from a form of TPF different than that which gives rise to the downfield absorptions.

The proton NMR spectrum of an ACN solution of TPF and perfluoroacetic acid (PFA) is given in Figure 37. The dramatic difference in the shapes of this spectrum and that of neutral TPF in ACN is proof that TPF is protonated by PFA. The two sets of peaks in the spectrum of the acid solution occur at approximately the same ppm as the peaks in the spectrum of neutral TPF. This finding suggests that the electron density on the phenyl rings in TPF$^+$ is about equal to that in neutral TPF.

The conclusions which may be drawn from the $^1$H NMR spectra presented are:

- TPF is deprotonated by TBAOH in DMSO solutions. This conclusion is proven by the dramatic change in the NMR spectrum which accompanies the addition of TBAOH to TPF solutions.

- TPF is protonated by PFA in ACN solutions. This conclusion is proven by the change in the NMR spectrum upon addition of PFA to TPF solutions.
FIGURE 37

$^1\text{H NMR Spectrum of Protonated TPF}$
- The charge density on the phenyl rings in TPFH⁺ and Li⁺TPF⁻ is approximately the same as that on the phenyl rings in neutral TPF. The evidence in support of this statement is the fact that the phenyl protons in TPFH⁺ and Li⁺TPF⁻ have NMR absorptions near those of neutral TPF.

- The charge density on the phenyl rings in TPF⁻ is higher than that on the phenyl rings in neutral TPF. This phenomenon is demonstrated by the overall upfield shift in the phenyl proton peaks which accompanies deprotonation.

- Deprotonated TPF in the presence of lithium is similar to neutral TPF and quite different from deprotonated TPF which is not associated with lithium. This finding is strongly supported by the similarities in the shape of the NMR spectra of TPF and Li⁺TPF⁻. The general shape of the spectrum of TPF⁻ is quite different from that of Li⁺TPF⁻. Additionally, the absorption peaks in the spectrum of Li⁺TPF⁻ occur at approximately the same energy as those in the TPF spectrum. The absorption peaks in the spectrum of TPF⁻ occur upfield from those in the Li⁺TPF⁻ spectrum.

- The phenyl portion of the spectra of TPF and Li⁺TPF⁻ are best explained in terms of two geometric forms of TPF. This statement is strongly supported by the fact that the NMR spectra of TPF in ACN and DMSO as well
as that of Li⁺<sub>-TPF</sub> contain four sets of phenyl peaks with area distributions of A:2A:B:2B. The fact that the line broadening found in the Li⁺<sub>-TPF</sub> spectrum for those peaks with areas of A and 2A is much greater than that found for those peaks with areas B and 2B also strongly supports the idea that the spectrum arises from two different forms of TPF.
Introduction to the CNDO Method

The total molecular energy of a molecule may be calculated from the equation

\[ E = \int \frac{\psi^* \mathcal{H} \psi}{\psi^* \psi} \, d\tau. \quad (1) \]

If the Born-Oppenheimer approximation is applied, i.e. if the nuclei are considered to be in fixed positions, then \( \mathcal{H} \) does not include the kinetic energy of the nuclei, and the Hamiltonian for a molecule with \( N \) nuclei and \( m \) electrons is given by

\[ \mathcal{H} = - \sum_{i=1}^{N} \frac{1}{2} \frac{\nabla_i \psi}{\psi} - \sum_{i=1}^{N} \sum_{\nu=1}^{M} \frac{z_\nu}{r_{i\nu}} + \sum_{i=2}^{N} \sum_{j<i}^{N-1} \frac{1}{r_{ij}}. \quad (2) \]

The first term is the kinetic energy of the electrons in atomic units. The second term is the interaction of each electron \( i \) with each nucleus \( \nu \). The charge of nucleus \( \nu \) is \( z_\nu \) and \( r_{i\nu} \) is the distance between electron \( i \) and nucleus \( \nu \). The third term is the interaction between the various electrons; \( r_{ij} \) is the distance between electrons \( i \) and \( j \).

If the molecular wavefunction \( \psi \) is approximated by a
single Slater determinant of orbital wavefunctions then by substituting Equations (2) and (3) into Equation (1)

\[ \Psi = \left| \psi_1 \psi_2 \psi_3 \cdots \psi_n \psi_n \right| \]  

and adding a term for the nuclear potential the energy of the molecule is given by

\[ E = 2 \sum_{i=1}^{n} H_{ii} + \sum_{i=1}^{n} \sum_{j=1}^{n} (2J_{ij} - K_{ij}) + \nu_n \]  

The first term is the sum of one-electron orbital energies.

\[ H_{ii} = \int \psi_i^*(1) H_{\text{core}}(1) \psi_i(1) \, d\tau \]  

\( H_{\text{core}} \) is that part of the molecular hamiltonian which corresponds to an electron moving through the field of the bare nucleus, i.e. the first two terms of Equation (2). The coulomb integral, \( J_{ij} \), accounts for the repulsion between two electrons in different orbitals.

\[ J_{ij} = \int \int \psi_i^*(1) \psi_j(2) \frac{1}{r_{ij}} \psi_i(1) \psi_j(2) \, d\tau_1 \, d\tau_2 \]  

The exchange integral, \( K_{ij} \), which arises from the Pauli principle, lowers the total energy.

\[ K_{ij} = \int \int \psi_i^*(1) \psi_j^*(2) \frac{1}{r_{ij}} \psi_j(1) \psi_i(2) \, d\tau_1 \, d\tau_2 \]  

The constant nuclear-nuclear interaction potential is given by

\[ \nu_n = \sum_{k=2}^{n} \sum_{k<n} \frac{Z_k Z_n}{r_{kn}} \]  

in which \( Z_k \) and \( Z_n \) are the charges on the \( k \) and \( n \) nuclei, and \( r_{kn} \) is the distance between the nuclei.

In practice it is too difficult to solve for the
orbitals $\psi_i$ without further approximation. The most common approximation is to treat the orbitals $\psi_i$ as a linear combination of atomic orbitals.

$$
\psi_i = \sum_{j=1}^{z} c_{ji} \phi_j \quad i = 1 \text{ to } n \quad (9)
$$

The orbitals $\phi_j$ form a basis set containing $z$ members.

If Equation (9) for the orbitals $\psi_i$ is substituted into Equation (4) for the energy of the molecule then the total energy of the molecule may be rewritten as

$$
E = \sum_{i,j} P_{ij} \mathcal{H}_{ij} + \frac{1}{2} \sum_{j,k} P_{ij} P_{kl} \left[ (ij|kl) - \frac{1}{2} (ik|jl) \right] + \nu_n
$$
in which

$$
P_{ij} = 2 \sum_{k=1}^{n} c_{ik} c_{ij},$$

$$
\mathcal{H}_{ij} = \int \phi_i(1) \mathcal{H}_{\text{core}} \phi_j(1) \, d\tau_1,$$

and

$$
(ij|kl) = \int \int \phi_i(1) \phi_j(1) \frac{1}{r_{12}} \phi_k(2) \phi_l(2) \, d\tau_1 d\tau_2.
$$

A valence basis set is used in CNDO calculations. One electron energies are calculated only for valence electrons. Inner shell electrons are treated as part of the core.\(^{25}\) The basic assumption in the CNDO method is that electron repulsion integrals involving overlap distributions are negligibly small. Using this zero differential overlap (ZDO) assumption one obtains

$$
(ij|kl) = (ii|kk) \delta_{ij} \delta_{kl}
$$
in which $\delta_{ij}$ is the Kronecker delta. Thus, only repulsion
integrals of the form \((ii|kk)\) are calculated.

The application of the ZDO approximation yields results that are not rotationally invariant. In order to remove the coordinate system dependence introduced by the ZDO approximation an assumption is made that \((ii|kk)\) depends solely on the atoms on which \(i\) and \(k\) are located. Thus

\[
(ii|kk) = \gamma_{AB}
\]

for all \(i\) on atom A and all \(k\) on atom B. The value \(\gamma_{AB}\) is the average repulsion between a valence electron on A and a valence electron on B.

Other approximations used in the CNDO method are discussed in detail elsewhere.\(^{25,10}\)

Calculational Results

In 1968 del Bene and Jaffe\(^ {26}\) modified the CNDO program for use in calculating electronic transition energies and oscillator strengths. The resulting CNDO/S program allowed calculations to be performed on molecules containing 31 or fewer atoms with a maximum of 100 basis orbitals. An LSU modified CNDO/S program, CNDO/S-2, which allows input of up to 99 atoms and 200 basis orbitals was used in this work.
The CNDO/S program ignores vibrational energy, therefore, transition energies predicted by CNDO/S should be compared with experimentally obtained energies for transitions between states which have no quanta of vibrational energy, i.e. 0-0, 1-0, 2-0 absorption bands. Since it is not possible to determine the energy of the 0-0 absorption in TPF, comparisons will be made between the wavelength of maximum absorption taken from a low temperature spectrum and the calculational results.

At room temperature in fluid solutions large, flexible molecules such as the formazans exist as a distribution of geometric isomers. Since the electronic properties of a molecule are dependent on the its geometry, calculations should be done for each geometric isomer. Unfortunately, this approach is not practical for the formazans. TPF in solution is known to exist as an equilibrium mixture of at least two geometric isomers.¹ The isomers are in U geometries: one of these isomers is somewhat twisted so that the formazan system is not planar. Additionally, there are probably many other geometric isomers in solution that differ from these two isomers only slightly. Among the isomers are the innumerable rotamers derived from rotation of the phenyl groups.

The results of CNDO/S calculations are commonly
interpreted in terms of $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions. A "pure" $\pi \rightarrow \pi^*$ transition contains contributions from only those p atomic orbitals which are perpendicular to the plane of the molecule. Similarly, "pure" $n \rightarrow \pi^*$ transitions contain no contribution from the p orbitals which are perpendicular to the plane of the molecule. Obviously, those terms as commonly used have no meaning when applied to nonplanar molecules. What is not obvious is that the CNDO/S program assumes a molecule is planar only when the molecules input coordinates place it in the $xy$, $xz$ or $yz$ plane. A planar molecule with input coordinates that are not zero in at least one dimension, i.e. rotated out of the axial planes, yields results which at first appear to show "mixing" of the $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions. The "mixing" is actually an artifact which arises from rotating the molecule out of the axial planes.

Results from this investigation indicate that the CNDO/S program is extremely sensitive to the degree of planarity of the molecule. A molecule which varies from planarity by only a few hundredths of an Angstrom may show a fairly high degree of "mixing". The terms $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ are ordinarily applied to results obtained before configuration interact (CI). During CI a limited degree of mixing between orbitals may occur so that the final results are described as pure $\pi \rightarrow \pi^*$, predominantly $\pi \rightarrow \pi^*$, etc.
Since many of the molecules examined in this work are nonplanar the terms type A transition and type B transition have been used. Type A transitions are similar to $\pi \rightarrow \pi^*$ transition: they are composed of atomic orbitals which are approximately perpendicular to a localized plane defined by an atom's bonding structure. Type B transitions are similar to $n \rightarrow \pi^*$ transitions: they are constructed from orbitals parallel to the localized bonding plane.

One of the problems in performing CNDO/S calculations on formazan derivatives is that the program will not achieve self-consistency when the usual default criterion for convergence is used. As the iterative routine which calculates the total energy approaches a self-consistent result the total energy calculated in each pass through the routine begins to oscillate about an average value. Previous work\(^1\) showed that the change in energy calculated in successive iterations is about an order of magnitude larger than the default convergence criterion. If the convergence criterion is relaxed by an order of magnitude self-consistency is achieved.

In order to examine the validity of results obtained under the relaxed convergence criterion calculations were performed on pyridine, the cyclic diazines and
sym-tetrazine. Input geometries for these compounds were created by means of the Alchemy program available from Tripos Associates. It was found that the geometries of molecules constructed from Alchemy varied by only a few hundredths of an Angstrom from their MM2.87 optimized geometries. The results of these calculations are presented in Table 2, along with CNDO/S results for pyridine and the cyclic diazines obtained by del Bene and Jaffe$^{26,27}$ who used the normal default convergence criterion and geometries from x-ray diffraction experiments. The experimental values shown in the table were taken from spectra of room temperature cyclohexane solutions$^{28}$ and from gas phase spectra.$^{26}$

The first conclusion that may be drawn from these results is that while the results calculated for this work are not as close to experimental value as those obtained by del Bene and Jaffe they are good enough to establish general trends. CNDO/S calculations ordinarily predict nitrogen based n→π* transitions at lower energies than those that are observed experimentally.$^{27}$ The same trend has been found for carbonyl based n→π* transitions in the β-diketones.$^{10,28}$ CNDO/S tends to predict π→π* transition energies that are too high.$^{10,27,28}$ Using the relaxed convergence criteria π→π* transition energies calculated in this work were 1100 to 1700 cm$^{-1}$ too low.
A second conclusion which may be drawn from these results is that CNDO/S does not do a good job of treating the interaction of carbon and nitrogen. The calculated n→π* transition energies are 3400 to 5000 cm\(^{-1}\) too low. It is clear from the results of the diazines that the position of the nitrogen atoms affects the quality of the results. Calculations were not performed on enough compounds to determine how the number and position of nitrogen atoms affect the calculations.

CNDO/S calculations were performed for a variety of formazan derivatives including:

- formazan,
- trimethylformazan (TMF),
- 1-phenylformazan (1-phenyl),
- 3-phenylformazan (3-phenyl),
- 1,3-diphenylformazan (1,3-diphenyl),
- 1,5-diphenylformazan (1,5-diphenyl),
- 5-methyl-1,3-diphenylformazan,
- 3-methyl-1,5-diphenylformazan, and
- triphenylformazan.

CNDO/S calculations for both TPFH\(^+\) and TPF\(^-\) were attempted. An oscillatory pattern different from that which occurs during calculations for neutral TPF was found to occur in calculations for both TPFH\(^+\) and TPF\(^-\). In the case of neutral TPF the total energy calculated by
the CNDO/S program oscillated about a constant average energy. In the calculations performed on the ionic derivatives the total energy oscillated about an average value which slowly drifted to lower energy. The rate of change of the average total energy of the molecule was too slow to allow the calculations to be performed in a reasonable amount of time for either TPFH\(^+\) or TPF\(^-\).

Optimized geometries obtained from MM2.87 were used as the input geometries in this set of CNDO/S calculations. A detailed review of the MM2 method used to generate input geometries is given elsewhere.\(^1\) It should be noted that these geometries define a single tautomer of the formazan system which does not have C\(_{2v}\) symmetry.

The results of the CNDO/S calculations for formazan derivatives with MM2.87 optimized geometries are shown in Tables 3 through 11. Experimental results for derivatives which have been studied in this or previous works are included in the tables. The information intended to be drawn from the calculational data is the nature of the electronic transitions in TPF and the effect of methyl and phenyl substituents on the electronic transitions of the formazan system.

All of the derivatives studied have a calculated low energy transition in the visible region. In formazan this
transition occurs at 608 nm. Before CI the low energy transition in formazan is type B. During CI extensive mixing occurs. The transition after CI is best described as a mixed transition with about 60% B character.

The nature of the low energy transition is the same for all the derivatives examined. The effects on this transition of adding methyl or phenyl substituents to the formazan ring are to add some oscillator strength to the transition and to alter the energy of the transition slightly. Both the number and type of substituents affects the energy of the transition. It is not possible from these data to separate the influence of the type of substituent from the influence of the position of that substituent on the formazan ring.

The fact that the calculated low energy transition of formazan is relatively unchanged by the addition of substituents to the formazan system indicates that the low energy absorption of TPF arises from the formazan system itself and is not dependant upon the presence of the phenyl rings.

The addition of a phenyl group to the formazan system causes the a strong type A transition to appear in the near UV between 340 nm for 3-phenyl and 390 nm for TPF. This transition does not exist in either formazan or TMF.
The transition involves ground state orbitals which are largely localized on the phenyl rings and excited state orbitals which are delocalized over the entire molecule. These results may be interpreted as indicating that the transition involves some charge transfer from the phenyl substituents to the formazan system.

There is a problem with these calculations: the input geometries are for formazan tautomers. There are distinct differences in the bond lengths between N1 - N2 bond in the N4 - N5 bond as well as between the N2 - C3 bond and the N4 - C3 bond. The MM2.87 calculated bond lengths for TPF are presented in Table 12. No scheme suitable for calculating the geometry of molecules as large as the formazan derivatives is capable of generating a ground state geometry which reflects the delocalization of the formazan system. A second problem in this set of calculations is that the geometry of the formazan system varies slightly from derivative to derivative. The orientation of the formazan substituents with respect to the formazan system also varies. The differences in the CNDO/S calculations, therefore, do not arise solely from the nature and placement of the substituents on the formazan system.

The presence of the hydrogen in the formazan ring creates a problem in calculating a delocalized geometry.
for the formazan system. Input to the MM2 program includes the atom types, positions and bonding pattern. An atom is assigned an MM2 "atom type" based on the number, type and geometry of the bonds connected to that the atom. For example, a nitrogen bonded to three atoms all of which lie in a plane has a different MM2 designation than a nitrogen atom bonded to three atoms in a pyramidal configuration. MM2 treats these two nitrogens as if they were entirely different atoms. Additionally, if one specifies that a hydrogen is bonded to two atoms the program crashes. The nature of the MM2 program is such that it is impossible for the program to calculate a geometry for a delocalized, C_{2v} formazan system. The fact that N1 and N5 are treated as different types of atoms affects both the bond length from these nitrogens to their substituents and the dihedral angle between the nitrogen substituents and the formazan system. The phenyl ring attached to N1 and the phenyl ring attached to N5 differ in their alignment with respect to the formazan ring.

The presence of the hydrogen bond also adversely affects MNDO calculations. Initial input to the MNDO program includes the position and atomic number of the atoms in a molecule. MNDO has an advantage over MM2 in that bonding is not input into the program. The input geometries of all formazan derivatives into MNDO were C_{2v}
with the hydrogen equidistant from N1 and N5. In the optimized, output geometries the hydrogen was asymmetrically positioned between N1 and N5 which is correct for a hydrogen-bonded hydrogen.

It is well known that a hydrogen-bonded hydrogen is not centered between the two atoms to which it is bound. A potential energy diagram of a hydrogen-bonded hydrogen bound to identical atoms, $X_1$ and $X_2$, looks like a parabola with an indentation, a slightly raised maximum, at the bottom. The minima on either side of the maximum are at equal energy. There is an equal probability of finding the hydrogen closer to one atom than the other. The equilibrium $X_1$-H bond length is equal to the equilibrium $X_2$-H bond length. The probability of finding the hydrogen centered between the atoms to which it is bound is lower than the probability of finding the hydrogen closer to one atom.

MNDO optimized geometries of formazan derivatives have asymmetrically positioned hydrogens. However, the MNDO program does not recognize hydrogen bonds. As a result, the program finds that N1 is bonded to H7, N2 and a phenyl ring carbon but N5 is only bonded to N4 and a phenyl ring carbon atom. The formazan system contains inequivalent nitrogen-nitrogen and carbon-nitrogen bonds. The resulting optimized geometries are nearly identical
to those obtained from MM2.87. Optimized geometries obtained from AM1 calculations were indistinguishable from those obtained from MNDO calculations.

If the electrons in the formazan system are delocalized then N1 and N5 must be electronically equivalent; N2 and N4 also must be equivalent. If the hydrogen is ignored then the symmetry of the planar U form of a delocalized formazan system is $C_{2v}$. At first glance it would appear that the inclusion of the hydrogen in the formazan system destroys the $C_{2v}$ symmetry but such is not the case; it is imperative to remember that the position of the hydrogen alternates between N1 and N5. The equilibrium bond length between N1 and the hydrogen atom is equal to the equilibrium bond length between N5 and the hydrogen. On a time scale longer than the rate of proton transfer between N1 and N5 the symmetry of the formazan system is $C_{2v}$.

A geometry for the formazan system which reflects $C_{2v}$ symmetry was created by averaging the bond lengths taken from MNDO calculations. All the angles in the formazan system were set equal to 120°. The hydrogen was placed equidistant from N1 and N5. If an axis was drawn across the formazan system through the center of the nitrogen-nitrogen bonds and the molecule was rotated 180° then the formazan hydrogen would be located in the
position occupied by C3 before rotation.

CNDO/S calculations were performed on formazan and the 1-methyl; 3-methyl; trimethyl; 3-phenyl; 1,3-diphenyl; 1,5 diphenyl; and triphenyl derivatives when the created, $C_{2v}$ geometries were used. The results of these calculations are shown in Tables 13 through 20.

The lowest energy electronic transition calculated for each derivative is a type B transition localized on the formazan system with a wavelength of absorption which varies from 1469 to 8660 nm (0.14 - 0.81 eV). This result is clearly incorrect. For each derivative the transition involves ground state non-bonding orbitals on N2 and N4 and excited state $\pi$ orbitals located on N1 and N5. In the case of formazan the difference in energy between the ground state orbital and the excited state orbital is 6.7 eV, for TPF the energy difference is 6.1 eV.

The transition energy is the sum of the difference in energy between the ground and excited state plus the difference in the exchange and repulsion integrals between the two states. Ordinarily the contribution of the exchange and repulsion integrals is fairly small, on the order of 1 eV. It is almost impossible for the exchange integral to make a 6 eV contribution to the transition energy. The source of the low transition
energy must lie with the repulsion integral. According to Kestner\textsuperscript{29} the only way to explain an extremely high repulsion energy is for the transition to involve an "excited state" orbital which is already occupied or for CNDO/S to attempt to form a bond between two atoms which involves the excited state orbital.

In general the transitions calculated for the derivatives with $C_2\nu$ geometry could be classified as $\pi\rightarrow\pi^*$ and $n\rightarrow\pi^*$ transitions. There is no mixing of $\pi$ and $n$ orbitals before CI. The exception is the 1-methyl derivative in which the $\pi$ and $n$ orbitals mix extensively before CI. It is interesting that only for this derivative does mixing occur. A CNDO/S calculation for 1-phenylformazan was attempted but the program would not converge.

The addition of a methyl substituent shifts the transitions of formazan to slightly lower energies and increases their oscillator strength. The relative ordering of the transition energies is affected by the location of the methyl substituent. For example there is a type A transition at 236 nm in the 1-methyl derivative. The same transition in formazan occurs at 153 nm; in 3-methyl formazan the transition occurs at 172 nm. The fourth lowest energy transitions of formazan and the 3-methyl derivative arise from the same orbitals. In the
1-methyl derivative the third and fourth transitions are reversed.

The most important result for formazan, the 1-methyl and 3-methyl derivatives is that the CNDO/S calculated results include transitions in the visible region. These type A transitions, located at 436 nm in formazan, 474 nm in the 3-methyl derivative and 491 nm in the 1-methyl derivative, arise from the formazan π cloud.

The three lowest energy transitions calculated for the 3-phenyl derivative arise primarily from the formazan system itself and are comparable to those calculated for formazan and the two methyl containing derivatives. There is a significant contribution to the first type A transition (487 nm) from the phenyl ring. The remaining transitions at wavelengths longer than 250 nm are distinctly different from those in derivatives that do not contain phenyl groups. These transitions arise from π orbitals on both the phenyl ring and the formazan system. There is a moderate amount of charge-transfer character in the 487 nm and 290 nm transitions. Electron density is shifted from the phenyl ring to the formazan system in these transitions.

The two lowest energy transitions of the diphenyl derivatives are quite similar to those found for the
1-phenyl and non-phenyl containing derivatives. There is an increased contribution from the phenyl $\pi$ clouds to the ground state orbital of the second transition. This contribution is reflected in the lowered energy and increased oscillator strength of the transition.

The location of the phenyl rings on the formazan system affects the energy, degree of mixing and oscillator strength of the transitions. In general, the type A transitions of the 1,3-diphenyl derivatives involve ground state orbitals comprised of $p$ orbitals from both the phenyl rings and the formazan system, and excited state orbitals largely localized on the formazan system. While there is a moderate degree of charge transfer character to most of the transitions, none of the transitions of the 1,3-diphenyl derivative is completely charge transfer in nature.

The second and third lowest energy transitions of the 1,5-diphenyl derivative contain a moderate degree of charge transfer character. The fourth lowest energy transition (306 nm) is a definite charge transfer transition. The ground state orbital contains contributions only from the two phenyl rings and the excited state orbital is localized on the formazan system. CND0/S calculates oscillator strengths of zero for pure charge transfer transitions. The fifth
transition (305 nm) should be degenerate with the fourth transition (306 nm). The ground state orbital contains a very small, about 3%, contribution from the \( p_z \) orbital on N5. In all other respects this ground state orbital is a mirror image of the ground state orbital in the fourth transition. The remaining transitions are best described as at least partially delocalized over the entire molecule.

The calculational result for TPF contains interesting information about the TPF molecule and the CNDO/S program itself. Table 20 shows all the calculated transitions after CI which have wavelengths longer than 250 nm. The transitions before CI are quite interesting. There are at least four pairs of transitions which should be degenerate that the program treats as nondegenerate. These transitions all have either ground or excited state orbitals derived from the \( p \) orbitals of the carbons atoms on the phenyl rings attached to N1 and N5.

All of the molecular orbitals which contain contributions from the orbitals on the carbons in the phenyl ring attached to N1 (phenyl 1) also contain contributions from the orbitals on the carbons in the phenyl ring attached to N5 (phenyl 3). If the TPF molecule has \( C_{2v} \) symmetry then phenyl 1 and phenyl 3 must be equivalent. The program should calculate pairs of \( \pi^* \)
orbitals arising from phenyl 1 and phenyl 3 which are degenerate. The program actually calculates $\pi^*$ orbitals which are only approximately degenerate; the calculated energies of "degenerate pairs" differ by about 0.01 eV.

The energies of transition from a single ground state orbital to the "degenerate pairs" differ by 0.02 eV to 0.17 eV and depend on which of the pairs is involved in the transition. Since the contributions from the atomic orbitals to the molecular orbitals in the "degenerate pairs" are not identical, the difference in the repulsion integrals between the ground and excited state orbitals are also not identical. The difference in the transition energies for the "degenerate pairs" is larger than the difference in the energy gap between the pairs.

During CI the differences in transitions to degenerate pairs is magnified. The fourth and sixth transitions calculated for TPF are predominantly composed of a transition from a "degenerate pair" of $\pi$ orbitals delocalized over phenyl 1 and phenyl 3 to the formazan system's $\pi^*$ orbital. Because the orbitals are not identical they mix with other orbitals slightly differently during CI. The transitions which result from the CI calculations differ by 0.22 eV. The lower energy transition (328 nm) is completely charge transfer in
nature and has zero oscillator strength. The higher energy transition is about 90% charge transfer in nature and has an oscillator strength of $1.4 \times 10^{-2}$.

The CNDO/S program allows the user to define the symmetry of an input molecule. It is advisable to specify the symmetry of a molecule in order to reduce the number of calculations the program must perform. The program would be forced to recognize the equivalence of phenyl 1 and phenyl 3 by specifying $C_{2v}$ symmetry in the input. Unfortunately, when the CNDO/S program was modified at LSU no alterations were made to the symmetry handling routines in the program. The program will not allow the input of symmetry parameters for the number of atoms in TPF.

The second transition (534 nm) calculated for TPF is largely localized on the formazan system but does contain some contribution from each phenyl ring. The nature of this transition is the same as the second transition calculated for formazan. The third, fourth, sixth and seventh transitions have significant charge transfer character. These transitions involve a shift of electron density from the phenyl rings to the formazan system.

The spectrum of TPF in a 3-methylpentane glass at 77K has transitions at 546, 503 and 478 nm. The 546 nm
transition has been attributed to the absorption of TPF in the planar U geometry. The calculated transition at 534 nm is surprisingly close to this value. The strong, near UV transition of TPF is split into two peaks at 343 and 330 nm in the 77K spectrum. There are calculated transitions for TPF at 332, 328, 314, 309 and 304 nm. The 77K spectrum has low intensity transitions at 364 and 350 nm.

There is a school of thought among some chemists that the only thing one gets from calculations of molecules is a collection of numbers. There are some merits to this belief; calculational results are not intrinsically probative and can be misleading. However, calculational results may be safely used in conjunction with experimental data to strengthen or weaken arguments which probe the nature of molecules.

The calculational results presented in this section suggest the following:

- The transition in the visible region of the TPF spectrum arises from the $\pi$ system on the formazan ring.

- The transition in the 300 nm region of the spectrum of TPF may be charge transfer in nature. Electron density shifts from the three phenyl rings to the formazan system.

- The transitions of formazan are lowered in energy
by the addition of methyl or phenyl substituents to the formazan system.

- The presence of phenyl substituents on the formazan system perturb the visible transition of formazan. The number and location of the phenyl substituents affect the intensity and energy of this transition.
DISCUSSION AND CONCLUSIONS

Assignment of Bands in the Spectrum of Neutral TPF

Prior to this study, no in depth theoretical investigation of the formazans had been reported. Crude Hückel\textsuperscript{31,32} and a few CNDO/S\textsuperscript{1} calculations had been published but were insufficient to investigate the nature of the absorption bands in formazans.

The CNDO/S results presented herein suggest the visible absorption band of TPF arises from the \( \pi \) cloud on the formazan system. The phenyl substituents on the formazan system shift the calculated transition from 492 nm in formazan to 534 nm in TPF, and increase the oscillator strength of the transition by an order of magnitude. Formazan is an unstable compound, therefore, no direct comparison may be made with experimental results. The published spectrum of 1,5-diphenylformazan in $\text{CCl}_3\text{H}$\textsuperscript{33} has a maximum absorbance in the visible region near 440 nm and a shoulder near 500 nm; the calculated visible transition for the $C_{2v}$ geometry of 1,5-diphenylformazan occurs at 508 nm. The wavelength of maximum absorption of TPF in $\text{CCl}_4$ occurs at 492 nm with a shoulder near 540 nm.
Ordinarily, planar isomers absorb to the red of nonplanar isomers.\textsuperscript{11,34,35} Since the calculations performed for 1,5-diphenylformazan and TPF used planar geometries comparisons should be made between the long wavelength shoulders in the absorption spectra and the CNDO/S results. The calculational results for both derivatives are surprisingly good; they suggest that there will be a band within 8 nm of the experimental values. More importantly, the trend in the calculational results mirrors the trend found in the experimental results. This agreement strongly suggests that the CNDO/S results are indicative of results that would be found. One may reasonably conclude that the visible transition in U forms of TPF arises from the $\pi$ orbitals on the formazan system.

The near UV, 300 nm, transition of TPF has been ascribed to a $\pi\rightarrow\pi^*$ phenyl ring transition that is red-shifted by the presence of the formazan system.\textsuperscript{1} This assumption is reasonable. The problem with this assignment is that neither the protonated nor deprotonated forms of formazan derivatives display an absorption near 300 nm. There is no reason for a phenyl ring transition to disappear upon protonation or deprotonation of the formazan system.
The CNDO/S results suggest that the near UV band of TPF may have charge transfer characteristics in which electron density flows from an occupied \( \pi \) orbital on the phenyl rings to a \( \pi^* \) orbital localized on the formazan system. This idea is consistent with the fact that the transition disappears upon protonation or deprotonation of the formazan system.

Charge transfer bands are ordinarily very intense and quite sensitive to solvent. The 300 nm transition is the most intense band in the spectrum of TPF in U geometries. The energy of the transition is not particularly sensitive to the polarity of the solvent.

Most molecules that have charge transfer transitions are more dipolar in the excited state than in the ground state. The more dipolar excited state is better solvated by polar solvents than the less dipolar ground state which causes a lowering of the energy of the excited state relative to the ground state. As a result, the charge transfer bands of such molecules shift to lower energies when the compounds are dissolved in increasingly more polar solvents. Some molecules with charge transfer bands have highly dipolar ground states and less dipolar excited states. The charge transfer bands of these
molecules shift to higher energies when the compounds are dissolved in increasingly more polar solvents. Solvent shifts associated with $\pi\rightarrow\pi^*$ charge transfer transitions are ordinarily much greater than those of non-charge transfer $\pi\rightarrow\pi^*$ bands.

It is possible for a charge transfer band to be unaffected by solvent polarity. If a molecule is somewhat dipolar in the ground state then charge transfer can reverse the direction of the dipole without affecting the net molecular dipole. In this case the solvation of the ground state would be similar to that of the excited state in both polar and nonpolar solvents. The energy of the charge transfer transition should be relatively unaffected by the polarity of the solvent.

The dipole moment of TPF is 2.76 D in dioxane solutions and 1.87 D in benzene solutions. The ground state of TPF is significantly dipolar. It is possible for TPF to have a charge transfer transition that is not affected by the polarity of the solvent. The fact that the 300 nm transition of TPF is not strongly affected by the polarity of the solvent does not preclude the possibility that the transition has significant charge transfer character.
The most compelling argument that the near UV transition is a charge transfer band is the absence of a transition near 300 nm in the spectra of ionic formazan derivatives. Intramolecular charge transfer involves the excitation of an electron localized on one portion of a molecule to an unoccupied orbital on a separate portion of the molecule. Anything that disrupts the normal electron distribution of the molecule should prohibit, or, at the least, significantly alter the energy of a charge transfer transition. For this reason a molecule's charge transfer bands generally disappear upon protonation or deprotonation of the molecule.11

Delocalization of the Formazan System

The formazan system in TPF has long been described as being tautomeric.2,13,14,36,37,38 This designation is meant to imply that the formazan exists as a system of distinct single and double bonds rather than as a delocalized system. Tautomerism in formazans should not be confused with the familiar enol-keto tautomerism of the ketones which involves migration of a hydrogen. Enol-keto type tautomerism in the formazans would consist of movement of H6 from N5 in the "enol" form to C3 in the "keto" form. Enol-keto tautomerism in the formazans is possible but has not been reported.
Early investigators believed that the formazan system was at least partially delocalized. These authors based their conclusions on the study of the IR spectrum of formazans and their metal complexes. Some authors appeared to advocate both positions at once. Schiele and Arnold stated in 1967 that only asymmetrically substituted triaryl formazans contained differentiable N-N and C-N bonds. In 1969 the authors modified their statements and concluded that symmetrically substituted triaryl formazans have distinguishably asymmetric electron distributions in the formazan system and that such formazans have differentiable single and double bonds. Oddly, in a companion paper Schiele and Arnold discuss the quasiaromatic nature of the formazan system. Quasiaromaticity implies delocalization of the formazan system.

Researchers who have advocated the position that the formazan system is tautomeric have based their arguments on IR, resonance Raman spectra, $^1H$ NMR spectra and visible absorption spectra. The data and arguments used to support this idea are examined below.

In their investigation of the $^{15}N$-$H$ coupling in
triaryl formazans Fischer et al.\textsuperscript{14} concluded that the formazan system could not be delocalized. These researchers found two $^{15}\text{N-H}$ coupling constants which they attributed to ortho positioned hydrogens coupled with a double bonded nitrogen and ortho positioned hydrogens coupled with a single bonded nitrogen. The $^{15}\text{N-H}$ coupling constants for TPF were not reported. That study occurred before Veas established the existence of two U forms of TPF; the authors assumed that the formazan system existed in only one geometry. Fischer's results are easily explained in terms of two geometries of TPF which have differing $^{15}\text{N-H}$ coupling constants. The fact that two coupling constants were found is not proof that the formazan system is tautomeric.

The most recent argument that TPF is a localized, tautomeric system is that of Lewis and Sandorfy.\textsuperscript{6} These researchers published a study of the IR and resonance Raman spectra of a set of $^{15}\text{N}$ labeled TPF compounds. In the resonance Raman spectra there is a band that clearly arises from an N-N stretch. The energy of the band is $1357 \text{ cm}^{-1}$ which the authors note is quite low for an N-N double bond. There is no band in either the IR or Raman spectra that could be attributed to an N-N single bond stretch. In the IR spectrum there is a band at $1551 \text{ cm}^{-1}$ which arises from the C-N double bond. No band in either
the IR or Raman spectra could be attributed to the C-N single bond stretch. Though the authors do not comment on the energy of the C-N stretch, 1551 cm$^{-1}$ is a very low energy for a C-N double bond stretch. The authors state that the low energy of the N-N stretch is probably "due to the intramolecular hydrogen bond and to some chelate ring resonance, although it is believed that the former has the largest effect."

Lewis and Sandorfy also investigated TPF derivatives which contained halogens in the para position of the phenyl ring attached to N1. In the resonance Raman spectra of the halogen derivatives the 1357 cm$^{-1}$ band is broadened and asymmetric. The resonance Raman spectrum of a bromine derivative which contained $^{15}$N in the N1 position, i.e. the brominated phenyl ring was bonded to $^{15}$N, has two N-N double bond stretches at 1359 and 1347 cm$^{-1}$. The lower energy band corresponds to the $^{15}$N-$^{14}$N stretch. The band at 1359 cm$^{-1}$, the $^{14}$N-$^{14}$N stretch, is significantly more intense than the 1347 cm$^{-1}$ band. This result was interpreted to mean that both the brominated derivative and TPF are tautomeric in nature.

The reasoning which lead to this conclusion is flawed. If TPF exists as a delocalized system then the potential well for the hydrogen bond is symmetrical. If
N1 and N2 are labeled with $^{15}$N and N4 and N5 are labeled with $^{14}$N then the resonance Raman should have two N-N stretches of equal intensity which arise from the stretching of $^{15}$N-$^{15}$N and $^{14}$N-$^{14}$N. These stretches should occur at significantly lower energy than those of isolated N-N double bonds; C-N stretches should also occur at lower energies than isolated C-N double bond stretches. These results were found in the Raman spectrum of the labeled compound.

If an electron-withdrawing substituent is attached to the phenyl ring on N1 then the average electron density of N1 and N5 will no longer be equal. The potential well for the hydrogen bond is no longer symmetrical; one side of the well will be deeper. The hydrogen will spend more time attached to one nitrogen than the other. The degree of delocalization of the formazan system will be lowered; the nitrogen to which the hydrogen is attached will appear to have less double bond character. This result was found by Lewis and Sandorfy.

The statement that the formazan $\pi$ system is totally delocalized means that if one could take an instantaneous photograph of the electrons in the formazan system the most probable result would be pairs of electrons which form the $\sigma$ bonds placed between the atoms with the $\pi$
electrons existing somewhere within the formazan system. Total delocalization implies that the probability of finding a \( \pi \) electron at any single position in the formazan system is equal to the probability of finding that \( \pi \) electron at every other position in the system.

The statement that formazan exists as tautomeric pairs means the formazan system consists of single bonds and double bonds. If the formazan system is tautomeric there are two equally probable pictures of electrons in the formazan system which differ only in the location of the double bonds. The probability of finding the electrons arranged as single bonds and double bonds is much greater than that of finding any other arrangement of the electrons in a tautomeric system.

In terms of IR and resonance Raman spectra the existence of tautomeric pairs implies the existence of distinct single and double bond stretches yet the spectra of Lewis and Sandorfy contain no bands from single bonds. The energies of the N-N and C-N stretches should be about the same as the energy of isolated N-N and C-N double bonds. The fact that the double bond stretching bands occur at very low energies indicates that TPF is highly delocalized. Lewis agrees that the IR and Raman spectra of non-brominated TPF may be interpreted in terms of a
delocalized formazan system. In fact, the spectra reported by Lewis and Sandorfy actually support the idea that the formazan system is delocalized.

The arguments of Avramenko and Stepanov that the UV-visible absorption spectrum of TPF demonstrates the tautomeric nature of TPF are unconvincing. These authors attributed the visible absorption band of TPF to the portion of the molecule shown in I; the near UV absorption was assigned to the portion of the TPF molecule shown in II. The spectrum of 1,5-diphenylformazan has an absorption near 300 nm, the same region that contains the near UV transition of TPF. Clearly, since the diphenyl derivative does not have a phenyl ring attached to C3 this assignment is incorrect.

The conclusions of Avramenko and Stepanov are made wholly questionable by the fact that their band assignments demand that the formazan system be delocalized. The only way that the entire formazan system
can act as a unit is if the system is delocalized. A localized, tautomeric, formazan system should have a near UV-visible absorption spectrum which is the sum of the absorptions of the three phenyl rings, the C=N and N=N units and the absorptions arising from the non-bonding orbitals on the nitrogen atoms. It is impossible for these chromophores to give rise to an absorption in the 500 nm region. The long wavelength absorption of azomethane occurs at 347 nm.\textsuperscript{44} The long wavelength absorptions of aniline and toluene are 280 nm and 261 nm respectively.\textsuperscript{45} Clearly the spectrum of TPF is not the sum of the absorptions of isolated phenyl rings and double bonds.

The \textsuperscript{1}H NMR spectrum of TPF discussed in a previous section is consistent with a delocalized formazan system. That spectrum contained four sets of phenyl peaks with area distributions of A:2A:B:2B. This spectrum is the anticipated one for a delocalized formazan system which exists in an equilibrium mixture of two U isomers. If the formazan system was tautomeric then a single U isomer of TPF would give rise to three sets of phenyl peaks with an area distribution of 1:1:1. A solution of tautomeric TPF which has a mixture of two U isomers would have an NMR spectrum in which there are six sets of phenyl peaks that would have an area distribution of A:A:A:B:B:B.
No data in the literature or in this work support the idea that the formazan system is tautomeric. The UV-visible, IR, resonance Raman and \(^1\)H NMR spectra of TPF are all best explained in terms of a delocalized formazan system which, in TPF, exists as an equilibrium mixture of at least two U isomers. It is impossible to explain these spectra in terms of tautomeric TPF.

Long Wavelength Absorption of the Diform Derivative

The visible absorption envelope of the U isomers of the diform derivative is considerably broader and less well defined than that of the U isomers of all other derivatives. The broadness of the absorption band is attributable to an increased amount of long wavelength, low energy, absorption by the diform derivative.

The diform derivative contains two formazan systems that are linked via a biphenylene bridge. Any absorption from the two formazans systems and biphenylene bridge acting as a unit should occur in the near IR, much further to the red than the long wavelength absorption found in the diform derivative. No absorption attributable to the two formazan systems and the
biphenylene bridge acting as a unit could be found by Lewis and Sandorfy\textsuperscript{2} in their study of a related diformazan. There must be another explanation of the long wavelength absorption in the diform derivative.

The possibility exists that the long wavelength absorption bands of the diform derivative arise from exciton or exciton-like splittings. The diform derivatives contains two formazan systems that are liked by a conducting bridge which would allow the flow of electrons between the two formazans. This interaction between the two formazans could give rise to low energy, long wavelength, transitions.

If there is a substantial flow of electron density between the two formazan systems then the photochromic behavior of the diform derivative should be significantly different than that of TPF. The bonds in the formazan system which acts as the donor should have somewhat less double bond character than those in TPF. The potential barrier between the \( \text{U} \) and \( \text{S} \) forms of the donor formazan system should be less than that for TPF. The \( \text{U} \) to \( \text{S} \) isomerization of the donor formazan should occur at lower energy than that of TPF. Similarly, the acceptor formazan in the diform derivative should have a higher electron density than the formazan system in TPF which should
increase the barrier to isomerization for the acceptor formazan. The U to \textit{S} isomerization for the acceptor formazan should occur at higher energy than that of TPF.

No detailed study of the photochromic behavior of the diform derivative has been performed. In their study of the photochromicity of the diformazan with a biphenylene bridge between nitrogen atoms Lewis and Sandorfy found that the photochromic behavior of diformazan was essentially identical to that of TPF. However, that study did not investigate the energy required for photoisomerization. Additionally, it should be remembered that the time required for movement of an electron through the biphenylene bridge is quite small. An experiment designed to probe the possible effects of interaction of the formazan systems on the photochromicity of diform would probably have to be conducted on at least a picosecond time scale.

The absorption spectra of TPF, naphthyl and diform in ACN and CCl\textsubscript{4} solutions are shown in Figures 38 and 39. The wavelength of maximum absorption in the visible region of the derivatives in both solutions increases in the order TPF < naphthyl < diform. It should be noted that the spectra of both TPF and naphthyl contain low intensity, long wavelength absorptions in the same area
FIGURE 38

Normalized Absorption Spectra of ACN Solutions Containing

a. —— TPF
b. —— Naphthyl
c. --- Diform
FIGURE 39

Normalized Absorption Spectra of ACN Solutions Containing

a. ——— TPF
b. ———— Naphthyl
c. . . . . Diform
as the intense, long wavelength absorption of diform.

The absorption envelope of biphenyl solutions extends to the red of that of benzene solutions; naphthalene solutions absorb to the red of both benzene and biphenyl solutions. Based upon the absorption spectra of benzene, naphthalene and biphenyl the wavelength of maximum absorption in the visible region should be ordered TPF < diform < naphthyl if the only interaction between the formazan system and its substituents in these derivatives is electronic.

If the long wavelength absorption of the diform derivative is not a result of exciton splitting then evidently the steric interaction between the formazan system and the biphenyl substituent is significantly different than that between the formazan system and the C3 phenyl substituent or the naphthyl substituent. Calculational results indicate that lowest energy geometry of biphenyl in the ground state has a dihedral angle between the rings of about 18 degrees. The lowest energy rotamer of a phenylformazan should have a dihedral angle between the phenyl ring and the formazan system which is slightly less than that of biphenyl; the repulsion between the ortho hydrogens in biphenyl should be greater than the repulsion between the ortho hydrogens.
of the phenyl ring and the nitrogens in the formazan system of a phenylformazan.

The steric interaction between a phenyl substituent and the formazan system should be about the same as that between the formazan system and the naphthyl substituent. Both have hydrogens in the ortho position. The fact that the ratio of S:U isomers in nonirradiated solutions of the naphthyl derivative is slightly greater than that of TPF may indicate that the steric interaction in the naphthyl derivative is somewhat greater.

Both TPF and the diform derivative have ortho hydrogens on phenyl rings which interact with the formazan system. Steric interactions in the diform derivative are complicated by the fact that the biphenylene bridge contains two phenyl rings that interact with each other as well as with the two formazan systems. It is possible that the interaction between the phenyl rings in the biphenylene bridge induces a decrease in the dihedral angle between the formazan systems and the phenyl rings in the biphenylene. The fact that the diform derivative absorbs to the red of both TPF and the naphthyl derivative suggests that the dihedral angle between the biphenylene phenyl rings and the formazan system is less than that between the formazan system and
the C3 phenyl ring in TPF or the naphthyl ring in the naphthyl derivative. More planar isomers ordinarily absorb to the red of less planar isomers.\textsuperscript{11,34,35}

The finding that the dihedral angle between the rings in the biphenylene bridge and the formazan system in the diform derivative is closer to zero degrees than the dihedral angle between the phenyl ring attached to C3 and the formazan system in TPF is not intuitively obvious. It seems more reasonable to assume that the dihedral angles in these compounds are similar. Intuitively, one might expect a dihedral angle near 15 degrees between one formazan system and the first phenyl ring in the biphenylene bridge, a second dihedral angle near 18 degrees between the two phenyl rings in the biphenylene bridge and a third dihedral angle near 15 degrees between the second phenyl ring in the biphenylene bridge and the second formazan system. The dihedral angle between the two formazan systems would then be either 18 degrees or 48 degrees.

If the dihedral angle between the biphenylene phenyl rings and the formazan system is equal to that between the phenyl and the formazan system in TPF then the problem of the red-shifted absorption of the diform derivative remains. The visible absorption of the diform
derivative will occur to the red of that of TPF and the naphthyl derivative if the formazan system in the diform derivative is more nearly planar than that in TPF or the naphthyl derivative. If the steric interaction between the phenyl rings and the formazan system in the diform derivative is similar to the steric interactions in TPF then the cause of a more planar formazan system in the diform derivative must be the electronic interaction between the biphenylene bridge and the formazan system. This possibility has already been ruled out because the control of geometry of the formazan system by electron interaction would require that the naphthyl derivative would absorb to the red of the diform derivative.

There are, thus, two possible explanations for the existence of the long wavelength absorption in the diform derivative. One explanation is the interaction between the two formazan systems which gives rise to exciton splitting. The second explanation is that the dihedral angle between the phenyl ring attached to C3 and the formazan system in the diform derivative is closer to zero than that in TPF. It should be noted that this explanation does not imply coplanarity of the phenyl rings in the biphenylene bridge.
Geometry of Protonated Derivatives

The spectra of the protonated derivatives contain strong bands in the 500 - 550 nm region. The wavelengths of maximum absorption in the visible region of Group One protonated derivatives are red-shifted 20 to 35 nm from those of the U forms of neutral derivatives. The shift in absorption energy is comparable to that which results from the protonation of neutral U isomers of the β-diketones to yield protonated U forms. These findings suggest that protonated forms of the formazans exists in U geometries.

The protonation of neutral S isomers gives the same product as the protonation of U isomers. Neutral naphthyl in the U geometry has a wavelength of maximum absorption at 490 nm in ACN solutions; the maximum absorbance of S isomers of naphthyl occurs at 403 nm in ACN solutions. The protonation of both U and S isomers yields a product which has a maximum absorbance at 512 nm. The wavelength of maximum absorption of the protonated form is shifted 22 nm to the red of that of the neutral U form, and 109 nm to the red of that of the neutral S form.

The shifts in the wavelength of maximum absorbance in the visible region that accompany protonation of Group
Two derivatives vary widely. The maximum absorbance of o-OH in MeOH shifts 100 nm to the red upon protonation. The 100 nm shift is close to the shift found upon protonation of S forms of the naphthyl derivative. The S geometry predominates when neutral o-OH is dissolved in MeOH. The wavelength of maximum absorption of o-OHH⁺ in ACN occurs 25 nm to the red of that of the neutral derivative while the maximum absorbance of o-OHH⁺ in CCl₄ is 11 nm to the blue of that of the neutral derivative in the same solvent. The U isomers of the o-OH derivative predominate in neutral ACN and CCl₄ solutions. The shift associated with protonation of the o-OH derivative in ACN is similar to that found for Group One derivatives; the shift associated with formation of o-OHH⁺ in CCl₄ is not.

Though the shifts in the wavelength of maximum absorbance that accompany the protonation of Group Two derivatives vary widely, all the spectra of protonated Group Two derivatives are quite similar to those of protonated Group One derivatives. The differences in the shifts accompanying protonation must arise from the differences in the geometries of the neutral derivatives, not from differences in the geometries of the protonated derivatives.

The shifts associated with the protonation of o-OH in
MeOH and ACN solutions are similar to those which accompany protonation of S and U forms of Group One derivatives. The 11 nm shift to the blue associated with the protonation of o-OH in CCl₄ solutions seems anomalous at first glance. It should be remembered that there are two neutral U isomers which absorb at two different wavelengths. In most solutions which contain U forms the isomer which absorbs at shorter wavelength predominates. However, in CCl₄ solutions the U isomer that absorbs at lower energy, longer wavelength, predominates. The predominance of the U form that absorbs at longer wavelength, probably the more planar U form, causes the 11 nm blue shift which accompanies protonation. The wavelength of maximum absorbance of o-OHH⁺ in CCl₄ is shifted approximately 30 nm to the red of wavelength of the short wavelength shoulder in the spectrum of the neutral derivative, a normal shift for protonated U forms.

The shift in the energy of maximum absorbance associated with the protonation of U forms of the formazan derivatives is similar to that associated with the protonation of U isomers of the β-diketones that form protonated U isomers. The shifts in the wavelength of maximum absorption which accompanies the protonation of S forms are approximately equal to the sum of the shift
associated with isomerization from the S form to the U form and the shift associated with protonation of U forms. All protonated formazan derivatives studied absorb in the 500 - 550 nm region. These facts support the conclusion that the absorption in the 500 - 550 nm region of the protonated derivatives arises from U protonated derivatives in U geometries.

There are at least two bands in the 500 - 550 nm region of the spectrum of protonated U forms. These two bands may arise from two different U isomers. It is also possible that only one U form exists for the protonated species; one of the absorption bands in the 500 - 550 nm region could be a vibrational band. The fact that the contour of the absorption envelope in the this region of the spectrum of the protonated derivatives is quite similar to the contour of the absorption envelope in the 485 - 525 nm region of the U forms of the protonated derivatives suggests, but does not prove, that there are two U geometries of the protonated derivatives.

Long Wavelength Absorption by Protonated Derivatives

All protonated derivatives absorb to some degree in the 600 - 650 nm region. This absorption is much more pronounced when the protonated derivatives are dissolved
in CCl$_4$. One clue to the source of this absorption may be found in the spectrum of CCl$_4$ solutions of the protonated diform derivative.

The spectra of TPFH$^+$, naphthylH$^+$ and diformH$^+$ in CCl$_4$ solutions are shown in Figure 40. The protonated form of the diform derivative, like the neutral derivative, has a much broader absorption envelope in the visible region than any other protonated derivative. There are at least three absorption bands in the spectra of TPFH$^+$, naphthylH$^+$ and diformH$^+$. The long wavelength absorption is much more intense in spectrum of the protonated diform derivative than in the other spectra of the other derivatives. Note that the wavelength of maximum absorbance associated with each absorption band changes very little from derivative to derivative. The relative intensities of the bands vary among the derivatives. The inflection point near 700 nm in the spectrum of diformH$^+$ coincides with the low intensity, long wavelength tail in the spectrum of naphthylH$^+$. This inflection point indicates the existence of a fourth absorption band in the spectrum of diformH$^+$.

The long wavelength transition of the protonated forms of all derivatives is most intense in spectra taken from CCl$_4$ solutions. Carbon tetrachloride, a nonpolar
FIGURE 40

Normalized Absorption Spectra of CC1₄ Solutions of

a. ——— TPFH⁺

b. ———— NaphthylH⁺

c. ······ DiformH⁺
Figure 40
solvent, solvates ions poorly. Perfluoroacetic acid was used to protonate derivatives dissolved in CCl₄. The perfluorooacetate anion is probably closely associated with the protonated formazans in CCl₄ solutions. If the perfluorooacetate anion is positioned over the formazan system extending beyond the edges of the formazan towards the phenyl rings then steric interaction between the anion and the phenyl ring will force the phenyl ring to be more nearly coplanar with the formazan ring. Protonated forms with more nearly coplanar phenyl rings should absorb to the red of those with less coplanar phenyl rings.

If the long wavelength absorption is due to steric interactions between the perfluoroacetate anion and the formazan substituents then the long wavelength absorption of all protonated derivatives should decrease when the derivatives are dissolved in more polar solvents. This result was found. The long wavelength absorptions of all protonated derivatives are far less intense in ACN and MeOH solutions than in CCl₄ solutions. Both ACN and MeOH solvate ions much better than CCl₄.

The long wavelength band which appears in the spectrum of the neutral diform derivative was discussed previously. Two possible explanations for the long
wavelength absorption were offered; one explanation was the existence of exciton splittings, the second explanation was increased coplanarity between the formazan system and the phenyl rings of the biphenylene bridge. The spectrum of protonated diform derivative in \( \text{CCl}_4 \) solution contains exceptionally long wavelength bands. The fact that the bands are coincident with lower intensity bands found in the spectra of \( \text{CCl}_4 \) solutions of \( \text{TPFH}^+ \) and \( \text{naphthylH}^+ \) suggests that the bands in all three spectra arise from coplanarity of the formazan system and its substituents.

There is another possible explanation for the intense long wavelength absorption of diform\( \text{H}^+ \). If only one of the two formazan systems in the diform derivative is protonated then the probability of an interaction between the two formazan systems is increased; electron density should flow from the non-protonated formazan to the protonated formazan along the conducting biphenylene bridge. An interaction between a protonated formazan and a neutral formazan should be stronger than the interaction between two neutral formazans. Such an interaction would give rise to a long wavelength absorption. If both formazan systems in the diform derivative are protonated then the interaction between the two formazans should be similar to that of the
neutral diform derivative.

Interestingly, the protonated diform derivative has exceptionally intense, long wavelength absorptions only when dissolved in CCl₄; the wavelength of maximum absorption of diformH⁺ in ACN solutions occurs at a shorter wavelength than that of naphthylH⁺ in ACN solutions. It is possible that in CCl₄ solution, which poorly solvates ions, that only one formazan in the diform derivative is protonated and that in ACN solution, which better solvates ions, both of the formazans in diform are protonated.

During the course of this work it was observed that the intensity of the long wavelength bands in the protonated forms of all derivatives appeared to be related to the nature of the solvent, the amount of acid present in the solvent, the rate of addition of the acid to the solvent and the amount of time between the addition of the acid to a solution and the recording of a spectrum of the solution. Studies designed to probe these effects were not successful because of complications from the photochemical reaction of protonated formazans.

Triphenylformazans in acidic solutions undergo a photochemical reaction to form tetrazolium salts.⁴⁷ In
the photochemical reaction bonds are created between N1 and N5 and between the phenyl ring attached to N1 and the phenyl ring attached to N5. The product of this reaction is a 3-phenyl-1,5-diphenylenetetrazolium salt. These salts absorb near 360 nm. A very low intensity band near 360 nm is found in the absorption spectrum of almost every protonated derivative reported in this dissertation. The photochemical reaction occurs whenever an acidic formazan solution is exposed to light of even extremely low intensity.

Geometry of Deprotonated Forms That Do Not Contain Li⁺

In the discussion of protonated forms it was noted that the 500 - 550 nm region of the spectra of all protonated forms was similar. The protonated derivatives were shown to exist predominantly in U geometries. The shifts in wavelength of maximum absorption that occurred upon protonation were found to be directly related to the geometry of neutral species.

In contrast, the spectra of deprotonated derivatives vary considerably from derivative to derivative and are affected by the nature of the solvent. The spectrum of a deprotonated derivative falls into one of two classes. One class of spectra is characterized by the appearance
of strong bands in the 500 - 550 nm region with some absorption near 450 nm. The intense band in the 500 - 550 nm region is narrower than the band associated with the absorption of neutral substances in U geometries. The second class of spectra is characterized by a broad absorption envelope that has a maximum absorbance in the 425 - 467 nm region. Spectra in this class have some absorption in the 500 - 550 nm region. The only spectra in the second class are those of CCl₄ solutions of the deprotonated o-OH and OH-Cl derivatives.

Neutral U isomers absorb in the 485 - 525 nm region; neutral S isomers of the same derivatives in the same solvents absorb in the 400 - 425 nm region. The shift in the wavelength of maximum absorption which accompanies U to S isomerization is usually 70 to 100 nm whether the isomerization is induced by irradiation or, in the case of the non-photochromic Group Two derivatives, occurs thermally.

The fact that the two regions in the visible in which the deprotonated derivatives absorb are separated by 80 to 100 nm suggests that deprotonated derivatives occur in U and S geometric isomers. The U isomers should absorb in the 500 - 550 nm region; the S isomers should absorb in the 425 - 470 nm region.
Deprotonation of Group One neutral U isomers yields a spectrum with a maximum absorption in the 500 - 550 nm region, 30 - 40 nm to the red of that of the neutral species. Assuming that U anions absorb in the 500 - 550 nm region, the red shift in maximum absorption associated with the deprotonation of neutral U isomers to form anionic U isomers is 30 - 40 nm. A similar shift in maximum absorption is found for the deprotonation of neutral U β-diketones which form U anions. This finding supports the conclusion that the absorption in the 500 - 550 nm region of the spectrum of deprotonated derivatives arises from U isomers.

Anions formed by the deprotonation of Group Two derivatives dissolved in polar solvents have maximum absorbances in the 500 - 550 nm region. The shifts which accompany deprotonation vary because the geometries of the neutral derivatives are solvent dependent. The wavelength of maximum absorption of o-Br occurs 112 nm to the red of that of the neutral in ACN solutions and about 100 nm to the red of the neutral in CCl₄ solutions. The S isomer of neutral o-Br and the U isomer of deprotonated o-Br predominate in both solvents. The maximum absorbance of o-OH in both ACN and DMSO solutions occurs in the 500 - 550 nm region.
Deprotonation of the o-OH derivative causes a shift to the red in the wavelength of maximum absorbance of 40 nm in ACN solutions and 132 nm in DMSO solutions. The U isomers predominate in neutral ACN solutions of o-OH; o-OH in DMSO solutions exists primarily as S isomers. The difference in the shifts in maximum absorption which accompanies deprotonation of o-OH in ACN and DMSO solutions is 92 nm, the same order of magnitude as the shift in maximum absorbance which accompanies S to U isomerization. These findings also support the conclusion that U anions absorb in the 500 - 550 nm region.

The wavelengths of maximum absorption of CCl$_4$ solutions of o-OH$^-$ and OH$^-$Cl$^-$ are 465 nm and 460 nm respectively. The maximum absorbance of the deprotonated forms occur about 70 nm to the blue of that of the neutral forms for both derivatives. The U isomer predominates in neutral CCl$_4$ solutions for both derivatives. Assuming that the absorption near 460 nm arises from anions in S geometries then the 70 nm shift represents the sum of the shift due to U to S isomerization and the shift caused by deprotonation.

The blue shift in maximum absorbance associated with U to S isomerization is 70 - 100 nm. The red shift associated with deprotonation of U neutral species which
form U anions is 30 - 40 nm. From these data the shift in maximum absorbance that would be expected for deprotonation of a neutral U isomer which forms an anionic S isomer would be of 40 - 70 nm to the blue. A 70 nm shift was found for deprotonation of both the o-OH and OH-Cl derivatives in CCl₄. This finding supports the conclusion that the absorption in the 460 nm region arises from anions in S geometries.

The fact that it is possible to form deprotonated formazans in S geometries is somewhat surprising. According to Arnold no deprotonated β-diketones in S geometries have been reported. After S isomers were found for the hydroxy containing formazan derivatives Arnold unsuccessfully attempted to form deprotonated β-diketones in S geometries by means of the method reported in this work.

It should be noted that the deprotonation of all the derivatives in CCl₄ was accomplished by addition of a methanol solution which contained TBAOH to the CCl₄ solution which contained a formazan derivative. Methanol is fairly insoluble in CCl₄; addition of more than a single drop, about 0.04 ml, of the basic methanol solution to the CCl₄ solution resulted in a two phase system.
Chemical intuition suggests that the deprotonated derivatives formed in CCl$_4$ are probably surrounded by a methanol solvent cage. This conclusion may well be true. However, the methanol solvent cage surrounding the deprotonated derivatives in the CCl$_4$ solutions cannot be the same as the methanol solvent cage surrounding the deprotonated derivatives in methanol solutions. Deprotonated o-OH and OH-Cl in CCl$_4$ solutions are yellow. Deprotonated o-OH and OH-Cl in MeOH solutions are purplish-red. If excess basic methanol is added to a CCl$_4$ solution which contains deprotonated O-OH or OH-Cl then a two phase system forms. The CCl$_4$ phase is yellow; the MeOH phase is red.

The spectra of deprotonated forms dissolved in MeOH solutions were not recorded. A very high concentration of base, at least 1.0 M, is required to deprotonate the formazans in methanol. Concentrated solutions of strong bases in alcohols will rapidly etch quartz cells. The absorption spectra of these solutions could be recorded in disposable glass cells.

**Effect of Li$^+$ on Deprotonated Formazans**

It was noted in Chapter 3 that the absorption
spectrum of the deprotonated derivatives is unaffected by the presence of all counter ions except Li⁺. Both the visible absorption and ¹H NMR spectra of deprotonated derivatives in solutions that contain Li⁺ are more similar to the spectra of the neutral derivatives than to the spectra of deprotonated derivatives in solutions which do not contain lithium.

The absorption spectrum of Li⁺TPF⁻ in DMSO contains two bands in the visible region and is reminiscent of the spectrum of neutral TPF. The maximum absorbance of Li⁺TPF⁻ occurs 5 nm to the red of that of TPF⁻ and 35 nm to the red of that of TPF. The phenyl absorptions in the NMR spectrum are consistent with the existence of two isomers of Li⁺TPF⁻. Clearly, both the NMR and visible absorption spectra support the conclusion that Li⁺TPF⁻ exists in an equilibrium mixture of two U isomers.

The ¹H NMR spectrum of deprotonated TPF in the presence of lithium is remarkably similar to that of the neutral species. The phenyl protons absorb at about the same energy in the solution containing lithium ion as those in the neutral derivative. This result indicates that the charge density on the phenyl rings in the derivative containing lithium is nearly identical with
that on the phenyl rings in the neutral derivative.

The fact that the charge density on the phenyl rings in the neutral and the lithium ion-deprotonated form does not necessarily imply that the charge on the formazan system is similar for both species. It was noted in the discussion of the NMR spectrum of protonated TPF that the charge density on the phenyl rings in the protonated derivative was similar to that in the neutral derivative. It is unlikely that the formazan system has the same charge density in the neutral, protonated and lithium ion-deprotonated forms of TPF.

The fact that the visible absorption of deprotonated TPF is narrow and appears to consist of only one absorption band combined with the fact that most cations do not affect that absorption indicates that deprotonated TPF is rigid. This finding is in accordance with the fact that the absorption spectrum of formazyl complexes is largely unaffected by the metal. The fact that Li\(^+\)TPF\(^-\) apparently exists in two U isomers suggests that TPF\(^-\) is less rigid when it is associated with Li\(^+\).

The interaction of TPF\(^-\) with Li\(^+\) must be different than the interaction of TPF\(^-\) with any other cation that was studied; the cations studied were Na\(^+\), K\(^+\), Rb\(^+\), Cs\(^+\),
Be$^{+2}$, Mg$^{+2}$, Ca$^{+2}$, Cu$^{+2}$, Co$^{+2}$, Ni$^{+2}$, Mn$^{+2}$, Zn$^{+2}$, Ce$^{+3}$ and several others. The question of the unique behavior of lithium cation relative to the properties of TPF$^-$ is a puzzling one. The crystal ionic radius of Li$^+$ is 60 pm, that of Mg$^{+2}$ is 65 pm and that of Be$^{+2}$ is 31 pm.$^{49}$ Neither Mg$^{+2}$ nor Be$^{+2}$ affects the spectrum of deprotonated TPF$^-$ which indicates that the size of the lithium cation cannot be the only factor.

Cotton states that many researchers have speculated on the sometimes peculiar effects associated with lithium.$^{50}$ According to Cotton, some researchers have suggested that lithium is capable of forming "hydrogen bonds" in some compounds. The results found in this work could indicate that the bonding between Li$^+$ the nitrogens in the formazan system of TPF$^-$ may be similar to that between H6 and the nitrogens in TPF. Though the designation Li$^+TPF^-$ has been used throughout this dissertation to denote the product which results from the addition of the lithium cation to deprotonated TPF it is possible that the bonding in this system is almost entirely covalent.

Summary

The data presented in this work support the following
conclusions:

- The formazan system in TPF is highly delocalized. This conclusion is supported by the fact that TPF absorbs in the visible region, the number of phenyl proton peaks and distribution of area under the peaks in the \textsuperscript{1}H NMR spectrum of TPF, and by the data contained in IR and resonance Raman spectra in the literature.

- The wavelength of maximum absorption of each form of the formazan derivatives examined in this study is dependent upon the geometry of the derivative, not upon the existence of a chelating hydrogen.

- The formazan derivatives examined in this work follow the same spectroscopic trends as the \( \beta \)-diketones. The shifts in the energy of maximum absorption which accompanies protonation, deprotonation and isomerization are of the same order of magnitude and in the same direction as those found for the \( \beta \)-diketones.

- Neutral formazan derivatives in U geometries ordinarily absorb in the 485 - 525 nm region. The spectrum of the diform derivative contains absorption bands at significantly longer wavelengths than those of the other derivatives studied. The long wavelength absorption of the diform derivative in U geometries probably arises from either an interaction between the two formazan systems of from molecules in which the biphenylene phenyl rings are nearly coplanar with the
formazan systems.

- The band in the visible region of the spectrum of TPF arises from a $\pi \rightarrow \pi^*$ transition of the formazan system.

- The absorption near 300 nm of neutral TPF and its derivatives is charge transfer in nature. The charge transfer transition probably involves ground state $\pi$ orbitals on the phenyl rings and excited state $\pi^*$ orbitals on the formazan system. This absorption either does not occur in ionic forms of TPF derivatives or occurs at significantly higher energy.

- The $^1$H NMR spectrum of TPF contains four sets of phenyl proton peaks. The distribution of the area under the peaks indicates that the spectrum arises from the absorption of phenyl rings on two different geometric isomers of TPF.

- Protonated derivatives studied in this work exist in U geometries. Protonated U derivatives usually absorb about 20 - 35 nm to the red of neutral U derivatives.

- All protonated derivatives have a long wavelength absorption band which is more intense in nonpolar solvents. This band coincides with the strong, long wavelength band found in the protonated diform derivative. The long wavelength absorption probably originates from isomers that have substituents that are nearly coplanar with the formazan system. Steric interaction between the formazan substituents and the
conjugate base of the acid used for protonation probably increase the percentage of isomers that have nearly coplanar substituents. The extremely long wavelength band in the spectrum of 
CCl₄ solutions of diformH⁺ may result from an interaction between the two formazan systems in a singly protonated molecule.

- The site of protonation in the derivatives studied is one of the nitrogens which is hydrogen bonded in the neutral derivative. This conclusion is supported by the fact that none of the protonated derivatives studied was photochromic.

- None of the deprotonated derivatives studied was photochromic. The lack of photochromicity in the deprotonated derivatives is probably due to an increase in the double bond character of the C-N bonds in the formazan system.

- The deprotonated derivatives exist in an equilibrium mixture of U and S geometric isomers. Deprotonated U isomers absorb in the 500 - 550 nm region; deprotonated S isomers absorb in the 425 - 470 nm region. Deprotonation of neutral U isomers to form anionic U isomers ordinarily causes a 30 - 40 nm red shift in the wavelength of maximum absorption in the visible region.

- The equilibrium between the U and S forms of deprotonated derivatives is dependent upon the substituents present on the formazan system and the
nature of the solvent. In general the U isomers predominate when an anionic derivative is dissolved in increasingly more polar solvents.

- Deprotonated derivatives are probably very rigid. This conclusion is suggested by the fact that only the lithium cation causes changes in the absorption spectrum of the anionic derivatives and by the fact that there is only one band in the visible region of the spectrum of the anionic derivatives.

- Li⁺TPF⁻ exists in an equilibrium mixture of two U geometries. This conclusion is supported by the absorption and ¹H NMR spectrum of the derivative.

Proposed Future Work

Resonance Raman studies would aid in determining the structure of the protonated forms. The resonance Raman spectrum of the U forms of TPF contain a band which is probably a ring breathing mode. Resonance Raman spectra could help determine if the formazan system in protonated TPF contains a double hydrogen bond.

Resonance Raman studies would also be useful for probing the nature of Li⁺TPF⁻. The results presented in this work suggest that lithium is probably chelated by TPF⁻. Carefully controlled studies designed to determine
if Li\textsuperscript{+}TPF\textsuperscript{-} is photochromic should be conducted. Very preliminary results with the o-Br derivative indicate that in DMSO solutions deprotonated o-Br in the presence of lithium exists in an equilibrium mixture of S and U isomers in which the S isomer predominates. These results suggest that the role of lithium in the formazan system is very similar to that of hydrogen.

\textsuperscript{15}N NMR studies of \textsuperscript{15}N labeled TPF should be performed. There were two attempts made to record the \textsuperscript{15}N NMR spectrum of TPF during the course of this research. It was found that the solubility of TPF in both DMSO and ACN was too low to allow the \textsuperscript{15}N spectrum to be recorded with compounds that contain only naturally abundant \textsuperscript{15}N. The \textsuperscript{15}N NMR spectrum of protonated TPF could be useful for determining the structure of that species. The \textsuperscript{15}N spectrum of Li\textsuperscript{+}TPF\textsuperscript{-} would also be useful in determining if that derivative is chelated. The chemicals necessary to synthesize the required nitrogen labeled compounds would cost about $1200.00 at the present time.

Studies of the singlet-triplet absorption in TPF and its derivatives should be undertaken. The existence of two singlet-triplet absorptions in the near IR would solidify the argument that there are two U geometries of TPF.
Remarks on the Importance of this Work

The β-diketones have been studied for many years by various researchers in the Nauman group at LSU. It has been generally believed, but not proven, that trends observed in the spectra of β-diketones may be used to explain the spectroscopy of other molecules which are capable of existing in more than one geometry. The study presented here confirms that belief. The work of those who investigated the β-diketones made interpretation of the spectra of the triphenylformazans much easier. This research extends the knowledge gained in the study of β-diketones on the effect of geometry on the electronic properties of neutral, cationic and anionic compounds.

In many ways the research presented in this dissertation is an historic anomaly. The absorption spectra reported in this work were recorded on a spectrophotometer which is older than the author of this dissertation. Most of the methods employed during the course of this research predate both the author and her major professor. With the exception of the $^1$H NMR spectra, all of the data presented here could have been gathered in 1930.
Although the instruments and techniques used in this study seem antiquated when compared with those used by many researchers the findings presented in this dissertation are important to contemporary chemists. Very little is known about the spectroscopy of organic ions yet organic ions are involved in nearly every biological process. Triphenylformazan itself is a biologically active molecule found in minute concentrations in a wide variety of organisms. The role of triphenylformazans in biological systems is largely unknown. The findings presented here should interest biochemists who work with systems containing formazans.

Most of the work done on large organic ions lies buried in the inorganic literature. No systematic study of the spectroscopy of organic ions has been undertaken. This work in conjunction with that done in this lab on the $\beta$-diketones and the dipyrromethenes is a small step in that direction.
<table>
<thead>
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<th>TPF in ACN</th>
<th>TPF in DMSO</th>
<th>Li+TPF- in DMSO</th>
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<td></td>
</tr>
<tr>
<td>8.129</td>
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All shifts are given in ppm.
### TABLE 2

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<th>$\lambda_{\text{max}}$</th>
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<td>288</td>
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<td>376</td>
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<td>243</td>
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<td>Pyrazine</td>
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<td>327</td>
<td>324</td>
<td>328</td>
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<tr>
<td></td>
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<td></td>
<td>260</td>
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<td>Tetrazine</td>
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The values in column one were calculated for this investigation.

The values in column two are calculational results of del Bene and Jaffe taken from reference 26.

The values in columns three and four are taken from reference 28.
### TABLE 3

CNDO/S Results for Formazan

**MM2.87 Geometry**

<table>
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<th>Transition</th>
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<th>Osc. Str.</th>
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<tr>
<td>Transition</td>
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<tr>
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<tr>
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<td>9.7 x 10^{-3}</td>
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TABLE 5

CNDO/S Results for 1-Phenylformazan

MM2.87 Geometry

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<th>Wavelength in nm</th>
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<td>324</td>
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<tr>
<td>A</td>
<td>304</td>
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TABLE 6

CNDO/S Results for 3-PhenylFormazan

**MM2.87 Geometry**

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<td>Transition</td>
<td>Wavelength in nm</td>
<td>Osc. Str.</td>
</tr>
<tr>
<td>------------</td>
<td>------------------</td>
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</tr>
<tr>
<td>Mixed B</td>
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<td>A</td>
<td>397</td>
<td>$5.1 \times 10^{-2}$</td>
</tr>
<tr>
<td>A</td>
<td>284</td>
<td>$1.9 \times 10^{-4}$</td>
</tr>
<tr>
<td>A</td>
<td>282</td>
<td>$1.5 \times 10^{-2}$</td>
</tr>
<tr>
<td>A</td>
<td>276</td>
<td>$8 \times 10^{-6}$</td>
</tr>
<tr>
<td>B</td>
<td>258</td>
<td>$4.9 \times 10^{-2}$</td>
</tr>
<tr>
<td>B</td>
<td>250</td>
<td>$1.9 \times 10^{-1}$</td>
</tr>
</tbody>
</table>
TABLE 8

CNDO/S Results for 1,3-Diphenylformazan

MM2.87 Geometry

<table>
<thead>
<tr>
<th>Transition</th>
<th>Wavelength in nm</th>
<th>Osc. Str.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mixed B</td>
<td>542</td>
<td>$3.4 \times 10^{-5}$</td>
</tr>
<tr>
<td>A</td>
<td>357</td>
<td>$3.5 \times 10^{-1}$</td>
</tr>
<tr>
<td>A</td>
<td>296</td>
<td>$1.8 \times 10^{-4}$</td>
</tr>
<tr>
<td>A CT</td>
<td>280</td>
<td>$1.1 \times 10^{-2}$</td>
</tr>
<tr>
<td>Mixed</td>
<td>272</td>
<td>$1.0 \times 10^{-3}$</td>
</tr>
<tr>
<td>A</td>
<td>263</td>
<td>$2.6 \times 10^{-1}$</td>
</tr>
<tr>
<td>Mixed</td>
<td>242</td>
<td>$3.2 \times 10^{-2}$</td>
</tr>
</tbody>
</table>
TABLE 9

CNDO/S Results for 3-Methyl-1,5-Diphenylformazan

MM2.87 Geometry

<table>
<thead>
<tr>
<th>Transition</th>
<th>Wavelength in nm</th>
<th>Osc. Str.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mixed B</td>
<td>654</td>
<td>2.8 x 10^{-3}</td>
</tr>
<tr>
<td>A</td>
<td>411</td>
<td>4.3 x 10^{-1}</td>
</tr>
<tr>
<td>A</td>
<td>287</td>
<td>2.1 x 10^{-2}</td>
</tr>
<tr>
<td>A</td>
<td>282</td>
<td>1.4 x 10^{-3}</td>
</tr>
<tr>
<td>A</td>
<td>277</td>
<td>3.2 x 10^{-3}</td>
</tr>
<tr>
<td>A</td>
<td>265</td>
<td>7.2 x 10^{-2}</td>
</tr>
<tr>
<td>A</td>
<td>255</td>
<td>2.2 x 10^{-1}</td>
</tr>
</tbody>
</table>
TABLE 10

CNDO/S Results for 5-Methyl-1,3-Diphenylformazan

MM2.87 Geometry

<table>
<thead>
<tr>
<th>Transition</th>
<th>Wavelength in nm</th>
<th>Osc. Str.</th>
</tr>
</thead>
<tbody>
<tr>
<td>B</td>
<td>544</td>
<td>5.3 x 10^-5</td>
</tr>
<tr>
<td>A</td>
<td>358</td>
<td>3.5 x 10^-1</td>
</tr>
<tr>
<td>A</td>
<td>297</td>
<td>2.6 x 10^-4</td>
</tr>
<tr>
<td>A</td>
<td>283</td>
<td>1.4 x 10^-2</td>
</tr>
<tr>
<td>A</td>
<td>272</td>
<td>1.4 x 10^-2</td>
</tr>
<tr>
<td>Mixed B</td>
<td>267</td>
<td>2.6 x 10^-1</td>
</tr>
<tr>
<td>A</td>
<td>246</td>
<td>3.6 x 10^-2</td>
</tr>
</tbody>
</table>
TABLE 11

CNDO/S Results for Triphenylformazan
MM2.87 Geometry

<table>
<thead>
<tr>
<th>Transition</th>
<th>Wavelength in nm</th>
<th>Osc. Str.</th>
</tr>
</thead>
<tbody>
<tr>
<td>B</td>
<td>684</td>
<td>$4 \times 10^{-6}$</td>
</tr>
<tr>
<td>A</td>
<td>427</td>
<td>$2.4 \times 10^{-1}$</td>
</tr>
<tr>
<td>A</td>
<td>349</td>
<td>$1.3 \times 10^{-5}$</td>
</tr>
<tr>
<td>A</td>
<td>296</td>
<td>$3.5 \times 10^{-1}$</td>
</tr>
<tr>
<td>A</td>
<td>283</td>
<td>$8.3 \times 10^{-2}$</td>
</tr>
<tr>
<td>A</td>
<td>271</td>
<td>$1.8 \times 10^{-1}$</td>
</tr>
<tr>
<td>Mixed B</td>
<td>265</td>
<td>$5.9 \times 10^{-3}$</td>
</tr>
</tbody>
</table>
Table 12

**MM2.87 Calculated Bond Lengths for Triphenylformazan**

<table>
<thead>
<tr>
<th>Bond</th>
<th>Length (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N1-N2</td>
<td>1.4930</td>
</tr>
<tr>
<td>N4-N5</td>
<td>1.3443</td>
</tr>
<tr>
<td>N2-C3</td>
<td>1.3383</td>
</tr>
<tr>
<td>N4-C3</td>
<td>1.3427</td>
</tr>
<tr>
<td>N1-H6</td>
<td>1.1138</td>
</tr>
<tr>
<td>N1-C&lt;sub&gt;phenyl&lt;/sub&gt;</td>
<td>1.3443</td>
</tr>
<tr>
<td>N5-C&lt;sub&gt;phenyl&lt;/sub&gt;</td>
<td>1.3438</td>
</tr>
<tr>
<td>C3-C&lt;sub&gt;phenyl&lt;/sub&gt;</td>
<td>1.3488</td>
</tr>
</tbody>
</table>
TABLE 13

CNDO/S Results for Formazan

C$_{2v}$ Geometry

<table>
<thead>
<tr>
<th>Transition</th>
<th>Wavelength in nm</th>
<th>Osc. Str.</th>
</tr>
</thead>
<tbody>
<tr>
<td>B</td>
<td>1956</td>
<td>0.0</td>
</tr>
<tr>
<td>A</td>
<td>436</td>
<td>$4.3 \times 10^{-2}$</td>
</tr>
<tr>
<td>B</td>
<td>364</td>
<td>0.0</td>
</tr>
<tr>
<td>Mixed</td>
<td>290</td>
<td>0.0</td>
</tr>
<tr>
<td>Mixed</td>
<td>212</td>
<td>$2.8 \times 10^{-2}$</td>
</tr>
<tr>
<td>A</td>
<td>200</td>
<td>0.0</td>
</tr>
<tr>
<td>B</td>
<td>193</td>
<td>$3.3 \times 10^{-1}$</td>
</tr>
</tbody>
</table>
TABLE 14

CNDO/S Results for 1-Methylformazan

C_{2v} Geometry

<table>
<thead>
<tr>
<th>Transition</th>
<th>Wavelength in nm</th>
<th>Osc. Str.</th>
</tr>
</thead>
<tbody>
<tr>
<td>B</td>
<td>2858</td>
<td>2.0 x 10^{-5}</td>
</tr>
<tr>
<td>A</td>
<td>491</td>
<td>6.3 x 10^{-2}</td>
</tr>
<tr>
<td>Mixed</td>
<td>374</td>
<td>1.2 x 10^{-4}</td>
</tr>
<tr>
<td>B</td>
<td>291</td>
<td>1.2 x 10^{-4}</td>
</tr>
<tr>
<td>A</td>
<td>236</td>
<td>8.5 x 10^{-3}</td>
</tr>
<tr>
<td>A</td>
<td>209</td>
<td>3.4 x 10^{-1}</td>
</tr>
<tr>
<td>B</td>
<td>202</td>
<td>3.4 x 10^{-3}</td>
</tr>
<tr>
<td>Transition</td>
<td>Wavelength in nm</td>
<td>Osc. Str.</td>
</tr>
<tr>
<td>------------</td>
<td>------------------</td>
<td>-----------</td>
</tr>
<tr>
<td>B</td>
<td>2211</td>
<td>0.0</td>
</tr>
<tr>
<td>A</td>
<td>474</td>
<td>5.3 x 10^{-2}</td>
</tr>
<tr>
<td>B</td>
<td>349</td>
<td>7 x 10^{-6}</td>
</tr>
<tr>
<td>Mixed</td>
<td>298</td>
<td>2.2 x 10^{-5}</td>
</tr>
<tr>
<td>Mixed</td>
<td>218</td>
<td>1.0 x 10^{-4}</td>
</tr>
<tr>
<td>B</td>
<td>205</td>
<td>8 x 10^{-6}</td>
</tr>
<tr>
<td>B</td>
<td>200</td>
<td>3.7 x 10^{-1}</td>
</tr>
</tbody>
</table>
### TABLE 16

**CNDO/S Results for Trimethylformazan**

*C₂ᵥ Geometry*

<table>
<thead>
<tr>
<th>Transition</th>
<th>Wavelength in nm</th>
<th>Osc. Str.</th>
</tr>
</thead>
<tbody>
<tr>
<td>B</td>
<td>8660</td>
<td>2 x 10⁻⁶</td>
</tr>
<tr>
<td>B</td>
<td>675</td>
<td>6.1 x 10⁻²</td>
</tr>
<tr>
<td>B</td>
<td>356</td>
<td>3.1 x 10⁻⁴</td>
</tr>
<tr>
<td>B</td>
<td>311</td>
<td>8.1 x 10⁻⁵</td>
</tr>
<tr>
<td>Mixed</td>
<td>268</td>
<td>5.2 x 10⁻³</td>
</tr>
<tr>
<td>Mixed</td>
<td>235</td>
<td>3.7 x 10⁻¹</td>
</tr>
<tr>
<td>A</td>
<td>233</td>
<td>5.0 x 10⁻³</td>
</tr>
</tbody>
</table>
TABLE 17

CNDO/S Results for 3-Phenylformazan

$C_{2v}$ Geometry

<table>
<thead>
<tr>
<th>Transition</th>
<th>Wavelength in nm</th>
<th>Osc. Str.</th>
</tr>
</thead>
<tbody>
<tr>
<td>B</td>
<td>1771</td>
<td>0.0</td>
</tr>
<tr>
<td>A</td>
<td>487</td>
<td>$5.1 \times 10^{-2}$</td>
</tr>
<tr>
<td>B</td>
<td>349</td>
<td>0.0</td>
</tr>
<tr>
<td>A CT</td>
<td>290</td>
<td>$5.9 \times 10^{-3}$</td>
</tr>
<tr>
<td>A</td>
<td>285</td>
<td>$3.4 \times 10^{-1}$</td>
</tr>
<tr>
<td>A</td>
<td>276</td>
<td>0.0</td>
</tr>
<tr>
<td>A</td>
<td>267</td>
<td>$2.3 \times 10^{-2}$</td>
</tr>
</tbody>
</table>
TABLE 18

CNDO/S Results for 1,3-Diphenylformazan

C<sub>2v</sub> Geometry

<table>
<thead>
<tr>
<th>Transition</th>
<th>Wavelength in nm</th>
<th>Osc. Str.</th>
</tr>
</thead>
<tbody>
<tr>
<td>B</td>
<td>2017</td>
<td>0.0</td>
</tr>
<tr>
<td>A</td>
<td>484</td>
<td>3.0 x 10&lt;sup&gt;-1&lt;/sup&gt;</td>
</tr>
<tr>
<td>A</td>
<td>315</td>
<td>0.0</td>
</tr>
<tr>
<td>Mixed</td>
<td>311</td>
<td>1.2 x 10&lt;sup&gt;-1&lt;/sup&gt;</td>
</tr>
<tr>
<td>A</td>
<td>306</td>
<td>1.7 x 10&lt;sup&gt;-2&lt;/sup&gt;</td>
</tr>
<tr>
<td>A</td>
<td>303</td>
<td>2.4 x 10&lt;sup&gt;-1&lt;/sup&gt;</td>
</tr>
<tr>
<td>A</td>
<td>281</td>
<td>8.5 x 10&lt;sup&gt;-3&lt;/sup&gt;</td>
</tr>
<tr>
<td>A</td>
<td>272</td>
<td>0.0</td>
</tr>
<tr>
<td>A</td>
<td>271</td>
<td>5.5 x 10&lt;sup&gt;-3&lt;/sup&gt;</td>
</tr>
<tr>
<td>A</td>
<td>260</td>
<td>6.5 x 10&lt;sup&gt;-2&lt;/sup&gt;</td>
</tr>
<tr>
<td>B</td>
<td>240</td>
<td>5.9 x 10&lt;sup&gt;-2&lt;/sup&gt;</td>
</tr>
</tbody>
</table>
TABLE 19

CNDO/S Results for 1,5-Diphenylformazan

C\textsubscript{2v} Geometry

<table>
<thead>
<tr>
<th>Transition</th>
<th>Wavelength in nm</th>
<th>Osc. Str.</th>
</tr>
</thead>
<tbody>
<tr>
<td>B</td>
<td>1469</td>
<td>0.0</td>
</tr>
<tr>
<td>A</td>
<td>508</td>
<td>4.0 x 10^{-1}</td>
</tr>
<tr>
<td>A</td>
<td>327</td>
<td>1.6 x 10^{-1}</td>
</tr>
<tr>
<td>A CT</td>
<td>306</td>
<td>0.0</td>
</tr>
<tr>
<td>A CT</td>
<td>305</td>
<td>1.0 x 10^{-4}</td>
</tr>
<tr>
<td>A</td>
<td>300</td>
<td>0.0</td>
</tr>
<tr>
<td>A</td>
<td>286</td>
<td>0.0</td>
</tr>
<tr>
<td>A</td>
<td>262</td>
<td>2.4 x 10^{-2}</td>
</tr>
<tr>
<td>B</td>
<td>261</td>
<td>3.7 x 10^{-2}</td>
</tr>
<tr>
<td>A</td>
<td>252</td>
<td>2.3 x 10^{-1}</td>
</tr>
<tr>
<td>B</td>
<td>243</td>
<td>7.1 x 10^{-2}</td>
</tr>
<tr>
<td>Transition</td>
<td>Wavelength in nm</td>
<td>Osc. Str.</td>
</tr>
<tr>
<td>------------</td>
<td>-----------------</td>
<td>----------</td>
</tr>
<tr>
<td>B</td>
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</tr>
<tr>
<td>A</td>
<td>534</td>
<td>$3.6 \times 10^{-1}$</td>
</tr>
<tr>
<td>A</td>
<td>332</td>
<td>$3.8 \times 10^{-1}$</td>
</tr>
<tr>
<td>A CT</td>
<td>328</td>
<td>0.0</td>
</tr>
<tr>
<td>A</td>
<td>314</td>
<td>$1.4 \times 10^{-1}$</td>
</tr>
<tr>
<td>A CT</td>
<td>309</td>
<td>$1.4 \times 10^{-2}$</td>
</tr>
<tr>
<td>A CT</td>
<td>304</td>
<td>$4.3 \times 10^{-3}$</td>
</tr>
<tr>
<td>B</td>
<td>299</td>
<td>$1.9 \times 10^{-3}$</td>
</tr>
<tr>
<td>A</td>
<td>276</td>
<td>$2.0 \times 10^{-3}$</td>
</tr>
<tr>
<td>A</td>
<td>276</td>
<td>$9.8 \times 10^{-3}$</td>
</tr>
<tr>
<td>A</td>
<td>270</td>
<td>0.0</td>
</tr>
<tr>
<td>A</td>
<td>261</td>
<td>$3.4 \times 10^{-2}$</td>
</tr>
<tr>
<td>B</td>
<td>256</td>
<td>$2.8 \times 10^{-1}$</td>
</tr>
</tbody>
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VITA

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Candidate: Elizabeth Wilhite

Major Field: Chemistry

Title of Dissertation: The Spectroscopy of Neutral and Ionic Forms of Triphenylformazan Derivatives

Approved:

[Signature]
Major Professor and Chairman

[Signature]
Dean of the Graduate School

EXAMINING COMMITTEE:

[Signature]

Date of Examination:
April 26, 1991