1972

Electronic-Spectroscopy of Highly-Polar Aromatics.

Omar Soliman Khalil
Louisiana State University and Agricultural & Mechanical College

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ELECTRONIC SPECTROSCOPY OF HIGHLY-POLAR AROMATICS

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

Omar Soliman Khalil
B.Sc., Alexandria University, Egypt, 1964
M.Sc., Alexandria University, Egypt, 1968
December 1972
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Finally, I acknowledge the moral support, encouragement, selflessness, spirit and tranquility of my wife Hoda during the years of my graduate work.
FOREWORD

The class of organic molecules which exhibits a relatively-large ground-state dipole moment is of immense proportions. In this dissertation a rather narrow segment of this large class (namely, molecules designated by the structure D-Ar-A, where D is an electron donor group, where Ar is an unsaturated ring system and where A is an electron acceptor group) will be discussed. We believe that these molecules are prototypical of the remaining members of the class of "highly-polar aromatics".

The electronic spectroscopy of D-Ar-A type molecules attracted the attention of many investigators, specially after the advent of the concept of charge transfer transitions [M. Godfrey and J.N. Murrell, Proc. Roy. Soc. (London), 273A, 71 (1964)]. A host of publications on the absorption spectroscopy of these molecules appeared; however, they dealt, for the most part, with the characterization of charge-transfer transitions, solvent and structural effects, determination of excited-state dipole moments, polarization and dichroic measurements, etc. The fluorescence spectra of some systems were investigated, specially in relation to solvation of different excited states and their dipole moments. However, it is a striking fact about these molecules that the existing set of total luminescence data is completely inadequate for interpretive purposes.

The main points of interest here are:

(1) The nature of the low-lying excited electronic states of these
molecules, and the effect of molecule and/or medium polarity on
electronic transitions involving these states.

(2) The effect of intermolecular dipole-dipole interactions of static
and transition moment types on the electronic spectra of these
molecules.

The material discussed in the first two chapters deals
with the first point. Total luminescence spectra of nitroanilines
are discussed. The \( \text{p-derivatives} \) show interesting luminescence
anomalies. A \( \varphi_p/\varphi_f \) dependence on N-methylation, solvent polarity
and exciting wavelength. Further, the lowest-energy absorption band
of the \( \text{p-derivative} \) shows dichroic effects upon N-methylation, upon
changes in solvent polarity and upon the application of electric
fields. The lack of adequate polarization data and computational
results prevents complete assignment of the electronic states or
quantification of the observed phenomena.

The material covered in the third and fourth chapters deal
with the second point of interest, namely dipole-dipole interactions.
The system studied was \( \text{N,N-dialkyl-p-cyanoanilines} \) which were report-
ed to show several fluorescences [E. Lippert, W. Lüder and H. Boos,
Proc. of The 4th International Meeting on Molecular Spectroscopy,
Bologna, Italy, (1959), Macmillian, New York p. 443, 1962; E.A.
Chandross and H.T. Thomas, Chem. Phys. Letters, 9, 397 (1971).]. The
nature and intensity of fluorescence emissions depend on temperature
and solvent polarity. Solvent reorientation during the lifetime
of the singlet excited state was suggested to explain the solvent and
temperature dependence of fluorescence intensities. In this system, we suggest that dipole-dipole interactions of static and transition moment type lead to the appearance of dimer (self-complex) and excimer emissions, in addition to the molecular (monomer) emission.
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ABSTRACT

The luminescences of isomeric nitroanilines and their N-methylated derivatives, as observed in glassy media at 77°K, are reported. The \( \sigma \)- and \( m \)- derivatives fluoresce only. The \( p \)-derivatives may fluoresce only, phosphoresce only, or show both a fluorescence and a phosphorescence whose relative intensities are dependent on the polarity of the medium and the exciting wavelength. Those \( p \)-derivatives which possess the largest ground-state dipole moments exhibit the largest phosphorescence yields; they also exhibit a dependence of \( \frac{\varphi_p}{\varphi_f} \) on excitation energies which lie within the wavelength compass of the lowest-energy absorption band, a "Red-Edge" effect, and different fluorescence and phosphorescence excitation spectra. Some suggestions as to the interpretation of these effects are made.

The absorption spectra of nitroanilines have been re-examined, with most emphasis placed on the lowest energy absorption band of \( p \)-nitroaniline. An increase of solvent polarity and/or N-methylation of \( p \)-nitroaniline shifts the lowest energy absorption band of this molecule to lower energies and uncovers a weak, structured, previously hidden transition at \( \sim 33000 \text{cm}^{-1} \). As the main absorption band moves to lower energies, a distinct preferential intensification occurs on its long-wavelength side. No such effects are observed for either the \( \sigma \)- or \( m \)-derivatives. The
data favour these theoretical models which predict that the lowest energy absorption band of the p-derivative encompasses two or more transitions.

The fluorescence spectra of N,N-dialkyl-p-cyanoanilines in fluid media have been reexamined. The long wavelength fluorescence, previously attributed to a solvated $^1L_a \rightarrow ^1A_1$ fluorescence, is interpreted as an excimer fluorescence, an assignment which is supported by concentration dependence studies and quenching experiments. The temperature dependence of the excimer/monomer fluorescence intensity ratio indicates that excimer formation is a diffusion controlled process. The binding energy of the excimer is found to be independent of the nature of the solvent and to be smaller than those values estimated for excimers of polycyclic aromatic hydrocarbons. Solvent viscosity, solvent polarity and specific solvent-solute interactions affect the excimer/monomer fluorescence intensity and these effects are interpreted. The geometry of the excimer is also discussed.

Finally the absorption and luminescence spectra of N,N-dialkyl-p-cyanoanilines in fluid and glassy media are reported. A weak absorption band at $\sim 29000 \text{cm}^{-1}$ is assigned to a self-complex of these molecules. Assuming a dimeric form for the self-complex, the association constant is $50 \leq K \leq 150 \text{ L/m}$. Excitation in the self-complex absorption region produces a phosphorescence and fluorescence which are at lower energies than the corresponding
monomer luminescences; the new emissions are assigned to $T^D_1 \rightarrow 1S^D_0$
and $1S^D_1 \rightarrow 1S^D_0$ events in the self-complex. The energies of, and
transition probabilities in the self-complex are rationalized
using a dimer stoichiometry and a model based on dipole-dipole
interactions of static and transition moment type.
CHAPTER I

LUMINESCENCE OF NITROANILINES
INTRODUCTION

The class of substituted aromatic molecules of structure D-Ar-A (where D is an electron-donor group, Ar is an unsaturated ring system and A is an electron-acceptor group) is characterized by highly-polar electronic excited states of relatively low energy. Such states are often referred to as intramolecular "charge-transfer" or "CT" states. The electronic spectroscopy of D-Ar-A molecules is neither well-investigated\(^1\) nor clearly understood.

This study is concerned with nitroanilines, a group of molecules which constitutes a sub-set of the D-Ar-A class. The emission spectroscopy of the nitroanilines has been touched on\(^2,3,4,5\) previously but no systematic experimental or theoretical approach seems to have been tried. It is known that the energies and intensities of the CT absorptive transitions in the nitroanilines vary in the order of \(p^- > m^- > o^-\) which, incidentally, is also the order of variation of the ground and excited state dipole moments. The subject of concern here is the somewhat unique emissive characteristics of the nitroanilines.

EXPERIMENTAL

All compounds were Eastman-Kodak products. They were recrystallized from dilute ethanol solution and/or multiply vacuum
sublimed until no change in emission spectra were obtained upon further purification. Sterically hindered nitroanilines were kindly provided by Professor Wepster (Technical University of Delft, Holland) and were used as received. Solvents were "fluorimetric grade" and were nonemissive at the level of experimental sensitivity needed in this work.

Emission spectra were corrected for the spectral response of the monochromator/phototube combination. Excitation spectra were corrected for lamp output and monochromator/phototube response. Phosphorescence decay processes were initiated by excitation with a millisecond pulse from an air-discharge lamp. All emission studies were restricted to thoroughly-degassed systems because non-degassed samples were found to have phosphorescence lifetimes which were approximately 10% less than those in deoxygenated solvents. Low temperatures were generated by direct immersion of sample in coolant.

Extreme care was taken to avoid inner-filter effects. Front surface excitation and low concentrations of the order of 2-5x10^{-6} M were used. Re-absorption of emitted light in the fluorescence/absorption overlap regions was estimated and was found not to exceed 1% of the emitted intensity under any of the experimental conditions used in this work.
RESULTS AND DISCUSSION

The emissive characteristics of the nitroanilines depend on several structural and experimental factors. We will list these factors and their effects and, thereafter, attempt interpretations based upon them.

(i) EFFECT OF SUBSTITUENT POSITIONS:

The o- and m- nitroanilines exhibit only a fluorescence in methylcyclohexane, EPA, ethylalcohol and methylcyclohexane glasses at 77°K whereas under similar conditions, p-nitroaniline exhibits only a phosphorescence. The corrected total emission spectra of these isomers are shown in Figure 1. Position isomers of N-methylated-nitroanilines behave similarly: N-methyl-o-nitroaniline, N,N-dimethyl-o-nitroaniline and N,N-dimethyl-m-nitroaniline fluoresce only; the p-isomers either fluoresce or phosphoresce or show both emissions depending on the polarity of the medium. In any event, the prevalence of phosphorescence in the p-isomers appears to be a common behaviour of all highly-polar aniline derivatives; for example, in the aminobenzoates and aminoacetophenones, \( \phi_p \) increases and \( \phi_f \) decreases as one proceeds through the isomeric series o- \( \rightarrow \) m- \( \rightarrow \) p-. The magnitude of ground-state dipole moments, changes in the static dipole moments produced upon excitation (as measured by solvent shifts) and excited-state dipole moments are also found to lie in the order p- \( \rightarrow \) m- \( \rightarrow \) o-, a trend which parallels the behaviour of the relative phosphorescence intensity exhibited in the luminescence spectra of the nitroanilines and which may be significant.
Corrected emission spectra of o-, m- and p-nitroaniline in EPA glass at 77°K. The total emission of the p-isomer consists solely of phosphorescence, that of the o- and m- derivatives consist solely of fluorescence.
(ii) **EFFECT OF N-METHYLATION:**

N-Methylation lowers the effective ionization potential of the amino group and makes it a better electron donor. It has a profound effect on the luminescence behaviour of p-nitroaniline. In the o- and m- series, changes of fluorescence intensity do occur upon N-methylation but the absence of absolute quantum yield data prohibits quantification of these changes. The important point here is that in the p- derivatives N-methylation induces a fluorescence where previously there has been none. The total luminescence spectra of p-nitroaniline and its N-methylated derivatives are shown in Figure 2.

(iii) **EFFECT OF SOLVENT POLARITY**

Emission spectra of nitroanilines are dependent on solvent polarity. For the o- and m- series, apart from fluorescence intensity changes which are not yet quantified, the only observed effect is that the fluorescence shifts to lower energy upon increasing the solvent polarity. In the p- derivatives, the following phenomena are observed:

--- The ratio of $\varphi_p/\varphi_f$ depends on the polarity of the medium. An increase of solvent polarity induces a fluorescence where there has been none or produces a fluorescence intensification, as shown by the following examples:

a. p-Nitroaniline phosphoresces only in methylcyclohexane, EPA and ethylalcohol glasses, but fluoresces weakly and phosphoresces strongly in highly-polar polyvinylalcohol films at 77°K.
Corrected emission spectra in EPA glass at 77°K, of PNA (p-nitroaniline), NMPNA (N-methyl-p-nitroaniline) and NNNDMPNA (N,N-dimethyl-p-nitroaniline). The phosphorescence is denoted P; the fluorescence, F.
RELATIVE INTENSITY

\[ \lambda (\text{Å}) \]

\[ \nu (\text{cm}^{-1} \times 10^{-3}) \]

F

P

[Diagram with molecular structures and intensity curves]
b. N,N-Dimethyl p-nitroaniline fluoresces very weakly in 3-methylpentane or not at all in methylcyclohexane at 77°K; on the other hand, fluorescence intensifies relative to phosphorescence in EPA and dominates completely in alcoholic glasses. In dimethylformamide and in polyvinylalcohol films at 77°K, the total emission consists of a strong fluorescence and a very weak, or even null, phosphorescence; indeed a very weak fluorescence is detectable even at room temperature in these last two media and has been reported previously for dimethylformamide solutions. The total emission spectra of N,N-dimethyl-p-nitroaniline are shown in Figure 3.

The phosphorescence lifetimes of the N-methylated-p-derivatives increase upon going from the hydrocarbon or EPA glasses to a wholly alcoholic glass (as shown in Table 1) but does not do so for p-nitroaniline itself. This behaviour is opposite to the trend of phosphorescence intensities which decreases upon going from EPA to an ethylalcohol glass.

The emission spectra are reasonably well-resolved in hydrocarbon glasses in contrast to those in either EPA or alcoholic glasses. A partial vibrational analysis of the phosphorescence emission of N,N-dimethyl-p-nitroaniline in methylcyclohexane is given in Table 2. A vibrational progression of 1330 cm$^{-1}$ appears weakly. The symmetric NO$_2$ stretching vibration of N,N-dimethyl-p-nitroaniline occurs at 1332 cm$^{-1}$ in carbon tetrachloride solutions and
Figure 3

Corrected emission spectra of N,N-dimethyl-p-nitroaniline in different solvent media at 77°K. The phosphorescence is denoted P and the fluorescence, F.

_____ in methylcyclohexane glass

----- in EPA glass

..... in polyvinylalcohol film
## TABLE 1

**MEAN PHOSPHOREScENCE LIFETIMES, \( \tau_p \), OF \( p \)-NITROANILINES**

IN FOUR GLASSY MEDIA AT 77°K

<table>
<thead>
<tr>
<th>Glass</th>
<th>( \mu^a ) (at 25°C)</th>
<th>PNA  ( \tau_p ) (sec)(^c)</th>
<th>NMPNA ( \tau_p ) (sec)(^c)</th>
<th>NNMPNA ( \tau_p ) (sec)(^c)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methylcyclohexane</td>
<td>0</td>
<td>---</td>
<td>0.24 ± 0.01</td>
<td>0.2 ± 0.04</td>
</tr>
<tr>
<td>3-Methylpentane</td>
<td>0</td>
<td>0.20 ± 0.02</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>EPA</td>
<td>0.81(^b)</td>
<td>0.24 ± 0.02</td>
<td>0.23 ± 0.05</td>
<td>0.22 ± 0.02</td>
</tr>
<tr>
<td>Ethylalcohol</td>
<td>1.36</td>
<td>0.24 ± 0.08</td>
<td>0.33 ± 0.07</td>
<td>0.35 ± 0.09</td>
</tr>
</tbody>
</table>

\(^a\) \( \mu \) denotes the dipole moment of the solvent in Debye units.

\(^b\) An "average dipole moment" representative of the mole fraction of the highly-polar ethylalcohol component.

\(^c\) These lifetimes refer to total phosphorescence intensity decay.
**TABLE 2**

**PARTIAL VIBRATIONAL ANALYSIS OF THE PHOSPHORESCENCE SPECTRUM OF N,N-DIMETHYL-\(p\)-NITROANILINE IN METHYLCYLCLOHEXANE GLASS AT 77°K**

<table>
<thead>
<tr>
<th>(\bar{\nu} (\text{cm}^{-1}))</th>
<th>(\Delta\bar{\nu} (\text{cm}^{-1}))</th>
<th>(\Delta\bar{\nu}/n (\text{cm}^{-1}))</th>
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</thead>
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<tr>
<td>21164</td>
<td>0.0</td>
<td></td>
</tr>
<tr>
<td>19802</td>
<td>1362</td>
<td>1362</td>
</tr>
<tr>
<td>18519</td>
<td>2645</td>
<td>1322</td>
</tr>
<tr>
<td>17241</td>
<td>3923</td>
<td>1307</td>
</tr>
<tr>
<td>Average</td>
<td></td>
<td>1330</td>
</tr>
</tbody>
</table>
decreases to 1320 cm\(^{-1}\) upon going to the more polar trichloroacetonitrile solvent. Since the asymmetric NO\(_2\) stretching frequency is 1506 cm\(^{-1}\) and the C=N stretching frequency is 849 cm\(^{-1}\), we may assign the 1330 cm\(^{-1}\) interval as a symmetric stretching frequency of the nitro group. A 400 cm\(^{-1}\) interval is also observed but cannot be assigned at present. In EPA glass, all \(p\)-nitroanilines show similar structure in their phosphorescence and fluorescence spectra. A 1100 cm\(^{-1}\) interval is recognizable in both the \(p\)-nitroaniline and the \(N\)-methyl-\(p\)-nitroaniline emission spectra and a very weak 900 cm\(^{-1}\) interval is present in the \(N, N\)-dimethyl-\(p\)-nitroaniline emission.

Since the diffuseness and overlap of the various peaks obscures the true values\(^1\) of the vibrational intervals, we assume here that the active vibration is, in all instances, the symmetric stretching frequency of the nitro group.

(iv) **EFFECT OF VARIATION OF EXCITATION ENERGY**

The emission spectra of \(o\)- and \(m\)-nitroanilines and their \(N\)-methylated derivatives are independent of excitation wavelength. The same is true of the emission spectrum of \(p\)-nitroaniline in methylcyclohexane, EPA and ethylalcohol glasses at 77\(^0\)K. However, in the case of \(p\)-nitroaniline in polyvinylalcohol films and \(N\)-methylated \(p\)-nitroanilines in EPA and ethylalcohol glasses, the \(\Phi_p/\Phi_f\) ratio depends on \(\lambda_{exc}\). Indeed, \(\Phi_p/\Phi_f\) decreases upon excitation on the extreme long-wavelength side of the lowest-energy absorption band.
Since, to a first approximation, we may write,

\[ \frac{\phi_p/\phi_f}{k_p/\phi_p} = \frac{k_p}{(k_p+k_q)} \frac{k_{isc}/k_f}{k_f} \]

it is implied that some one or all of the kinetic parameters is a function of \( \lambda_{exc} \). The most likely candidate is the intersystem crossing rate constant parameter, \( k_{isc} \).

Plots of \( I_p/I_f \) versus excitation energy are shown in Figure 4. In the three instances shown, \( I_p/I_f \) increases dramatically and reattains stability as \( \lambda_{exc} \) sweeps through the first absorption band. The frequency interval over which the \( I_p/I_f \) surge occurs varies in the order \( \Delta\nu_{(NMPNA)} < \Delta\nu_{(NNDMPNA)} \); there is, of course, no such surge in PNA itself.

Polarized absorption spectra of PNA and its N-methyl derivatives indicate that the lowest-energy (i.e., first) absorption band contains at least two different electronic transitions.\(^{11,12}\) In view of this and our prior assumption of an \( I_p/I_f \) sensitivity intrinsic to \( k_{isc} \), we may suppose that:

-----The rate constant \( k_{isc} \) is constant in both the \( S_1 \) state and the \( S_2 \) state but varies in the region between these pure states.

-----\( k_{isc} \) is larger in the \( S_2 \) state than in the \( S_1 \) state.

-----\( k_{isc} \) decreases with solvent polarity.

The totality of these evidences and assumptions suggests that \( S_2 \) is coupled more strongly to the triplet manifold than is \( S_1 \) and that \( S_1 \) is also coupled by some mechanism to \( S_2 \).
Figure 4

a) A plot of $I_p/I_f$ versus excitation energy for N-methyl-p-nitroaniline in EPA glass at 77°K

b) Similarly for N,N-dimethyl-p-nitroaniline

c) Similarly for 2,N,N-trimethyl-p-nitroaniline

Intensities were corrected for phototube/monochromator response and for lamp output at each exciting wavelength.
(a) 

(b) 

(c) 

(d)
(v) EXCITATION SPECTRA:

The fluorescence excitation spectra of N-methylated p-nitroanilines are slightly "red-shifted" with respect to the phosphorescence excitation spectra as shown in Figure 5. These red shifts increase as the polarity of the medium increases on going from EPA to ethylalcohol - an observation which is fully supportive of the suppositions of item (iv). The fluorescence and phosphorescence excitation spectra are different, that of fluorescence being biased towards the $S_1 \leftrightarrow S_0$ absorption act and that of phosphorescence being biased towards the $S_2 \leftrightarrow S_0$ absorption act (which, we suggest are both encompassed by the lowest-energy absorption band of the $p$-derivatives).

(vi) FLUORESCENCE - ABSORPTION MIRROR-IMAGE RELATIONSHIP:

The fluorescence band is not a good mirror-image of the lowest-energy absorption band of N-methylated p-nitroaniline as shown in Figure 6 for the case of EPA glass. The same behaviour is also found in ethylalcohol glass but the absence of fluorescence in hydrocarbon glasses precludes a similar comparison. This non-mirror image behaviour is not unexpected since the absorption band has been supposed to comprise two different electronic absorptive events whereas only the reverse of one of these processes is held responsible for the fluorescence.

(vii) THE "RED-EDGE" EFFECT

There is a slight but definite red-shift in the emission spectra of all N-methylated p-nitroanilines when excited at the extreme
red edge (i.e., low-energy side) of the first absorption band. This
effect is shown in Figure 7. It is smaller --- perhaps even absent ---
in the fluorescence emission but readily observable in phosphorescence.
Such a phenomenon, dubbed "The Red-Edge Effect," has been observed
for a wide range of aromatic compounds\textsuperscript{13} and is found to be larger
for polar molecules in polar media.\textsuperscript{14} This effect can be interpreted
in different ways:

\begin{itemize}
\item Microcrystalline effects, as in case of pyrazine in frozen
\begin{itemize}
\item solutions:\textsuperscript{15} However, since the luminescence of N,N-dimethyl-p-
nitroaniline crystal is different from that of glassy solutions,
\end{itemize}
\begin{itemize}
\item being composed only of a fluorescence somewhat similar to that
\end{itemize}
\begin{itemize}
\item which is observed in highly-polar dimethylformamide and polyvinyl
\end{itemize}
\begin{itemize}
\item alcohol at 77\textdegree{}K, this possibility may be eliminated.
\end{itemize}
\item Different solvated species, as in case of Michler's ketone:\textsuperscript{16}
\begin{itemize}
\item Since we were unable to detect different absorbing species in the
\end{itemize}
\begin{itemize}
\item absorption spectra of nitroanilines in various organic glasses, we
\end{itemize}
\begin{itemize}
\item feel obliged to eliminate this possibility also.
\end{itemize}
\item Dimer or polymer formation: Since the phenomena described here
\begin{itemize}
\item are independent of concentration in the range $10^{-3} \geq [\text{NNDMPNA}] \geq$
\end{itemize}
\begin{itemize}
\item $10^{-7}$ m/\textmu{}, it does not appear reasonable to suggest such a
\end{itemize}
\begin{itemize}
\item mechanism.
\end{itemize}
\item Full solvent relaxation in the $T_1$ state: We prefer this last
\begin{itemize}
\item supposition. In other words, we suppose that the red-edge
\end{itemize}
\begin{itemize}
\item exitation selects that ensemble of molecules which are solvent
\end{itemize}
caged in such a way as to provide the minimum energy for the T$_1$
state.
Figure 5

Corrected phosphorescence and fluorescence excitation spectra for N,N-dimethyl-p-nitroaniline in EPA glass at 77°K.
Figure 6

Arbitrarily - normalized and corrected fluorescence and absorption spectra of N,N-dimethyl-p-nitroaniline in EPA glass at 77°K.
Figure 7

The "Red-Edge Effect" exemplified in the emission spectrum of N,N-dimethyl-p-nitroaniline in EPA glass at 77^°K.

---excited at 380 m\(\mu\)

----excited at 420 m\(\mu\)
CONCLUSIONS

The conclusions of this work are rather straightforward and relate to a set of experimental observations for which we cannot as yet provide any definitive interpretation. Nonetheless, we can make a few rather plausible assertions. These are:

(1) For nitroanilines, as well as other sub-sets of D-Ar-A molecules, the phosphorescence intensities as well as the intersystem crossing efficiencies vary in the order $\sigma^- > \pi^- \approx \pi^-$, a trend which parallels that of the static dipole moments of both the ground and CT excited states and which may be significant.

(2) Polarized absorption measurements indicate that the lowest-energy absorption band in the $\pi^-$ derivative contains at least two differently-polarized transitions. The corresponding bands in the $\sigma^-$ and $\pi^-$ derivatives contain, as far as is known, only one electronic transition. In the specific case of $p$-nitroaniline, the two low-energy singlet states appear to be almost degenerate. If so, it may be supposed that in PNA the excitation energy transfers so rapidly to the triplet manifold that only a phosphorescence emission results. N-Methylation of $p$-nitroaniline may be supposed to decrease the efficiency of intersystem crossing to a point where fluorescence becomes observable, a supposition that could, in turn, be associated with a removal of the near-degeneracy of $S_1$ and $S_2$ states.
(3) In N-methylated-p-nitroaniline, ϕ_p/ϕ_f is a function of λ_{exc} when excitation is internal to the first absorption band. The sensitivity to solvent polarity, the "red-shift" of the fluorescence excitation spectrum relative to the phosphorescence excitation spectrum and the lack of a mirror-image relationship between fluorescence and absorption seem to indicate that S_2 is coupled more strongly to the triplet manifold than is S_1 and that S_1, in turn, is coupled by some mechanism to S_2.

(4) It is assumed here that the intervention of nπ* states may be neglected. This is a debatable supposition. If the 1nπ* state is of sufficiently low energy so that the 1Γ_{nπ*}+S_0 excitation is occluded in the lowest-energy absorption band of the nitroanilines, it is clear that some of the effects observed in this work could find interpretation along the well-worn lines of 1Γ_{nπ*}, 1Γ_{ππ*} state inversions. However, it is equally important to note that all of the effects observed here cannot be interpreted along such lines.

(5) Nitroanilines are highly dipolar. The emissive behaviour is highly sensitive to substitution effects which greatly alter the polarities of the various electronic states and to solvent effects which alter the energies of the various electronic states. Therefore, it seems reasonable to suppose that the primary effects under way relate to a mixing of S_1 and S_2 states, or vibronic states based thereon, produced by the field of the solvent dipoles and/or to modulations of the intersystem crossing process produced by solvent
and substituent alterations of the relative energies of $S_1, S_2$
and $T_1, T_2, \ldots$ states.
REFERENCES

(6) C. J. Seliskar, unpublished data.
(7) P. Suppan, J. Chem. Soc. (London), 3152 (1968). We consider solvent-shift measurements to grossly overemphasize the change in static dipole moment which occurs on going from $S_0$ to an $S_1$ excited state. Nonetheless, we believe that such values of $\Delta \mu$ are relatively correct and that, as long as no emphasis is placed on the quoted numeric values, they can be used with confidence for correlative purposes.¹


CHAPTER II

ABSORPTION SPECTRA OF NITROANILINES
INTRODUCTION

Despite the fact that the absorption spectra of the class of highly-polar aromatic molecules represented by the structure D-Ar-A (where D is an electron donor group, Ar is an unsaturated ring system and A is an electron acceptor group) have been extensively studied, the electronic spectroscopy of these molecules is not understood. Part of our lack of comprehension may be due to a scarcity of luminescence spectral data and the poor quality and diverse sources of absorption spectral data.

Nitroanilines are the most studied sub-set of this class of highly-polar aromatics. Spectroscopic data on these systems are scattered in various parts of the literature and are usually discussed with regard to substituent effects on the benzene spectrum, the relevance of intramolecular charge-transfer interaction concepts, electrically-induced dichroism, etc. Nonetheless, our overall understanding remains primitive.

Compounds, solvents and all experimental techniques used here are described elsewhere.

RESULTS AND DISCUSSION

The lowest-energy absorption band system of nitroanilines shifts to lower energies upon N-methylation and upon increasing the polarity of the medium. Those of the o- and m- derivatives do not change their absorption profile as they move to lower energies. That of the p- derivative exhibits a preferential intensification on its long-wavelength side as it moves to lower energy. These
effects are illustrated in Fig. 1 for p-nitroaniline.

The intense 31000 cm\(^{-1}\) absorption band uncovers a weak shoulder, at 33000 cm\(^{-1}\) (\(\varepsilon \approx 2 \times 10^3 \, \text{g cm}^{-1} \text{ m}^{-1}\)), as it moves to lower energy. This shoulder appears as a separate, weak, structured band in EPA glass at 77\(^0\)K, as is shown in Fig. 2. Neither the energy or intensity of this band appears to be sensitive to N-methylation or to any change of solvent polarity. This \(\sim 33000 \text{cm}^{-1}\) band has also been observed in the solution spectrum of N,N-dimethyl-p-nitroaniline\(^{10}\), and in the crystal absorption spectrum of p-nitroaniline\(^{16}\). It has been suggested\(^{16}\) that the \(\sim 33000 \text{cm}^{-1}\) is attributable to an \(1\Gamma_n \pi \pi^* \leftrightarrow 1\Gamma_1\) transition which borrows intensity from nearby \(\pi \pi^*\) states. However, this band is much too intense to justify such an assignment and, in addition, it does not show the familiar solvent sensitivity which is so characteristic of \(1\Gamma_n \pi \pi^* \leftrightarrow 1\Gamma_1\) transitions\(^{19}\). Whether the \(\sim 33000 \text{cm}^{-1}\) absorption band is an in-plane, short-axis polarized \(1\Gamma_n \pi \pi^* \leftrightarrow 1\Gamma_1\) transition or a \(1\Gamma_n \pi \pi^* \leftrightarrow 1\Gamma_1\) transition cannot be deduced at the moment; however, if it is \(1\Gamma_n \pi \pi^* \leftrightarrow 1\Gamma_1\), a very strong vibronic coupling must be present.

Electrodichroic absorption studies\(^{17,20}\), in methyl-cyclohexane solutions, on the \(\sim 31000 \text{cm}^{-1}\) absorption band of p-nitroaniline and on the corresponding, red-shifted 28000 cm\(^{-1}\) absorption band of N,N-dimethyl-p-nitroaniline indicate that this intense band encompasses two transitions: A long-axis polarized, intense transition (\(\varepsilon > 10^4\)), and a weak, short-axis polarized transition (\(10^3 < \varepsilon < 10^4\)). The shoulder at 33000 cm\(^{-1}\) does not
Absorption Spectra of \( p \)-nitroaniline and its \( N \)-methylated derivatives at 25\(^\circ\)C.

(a) \( p \)-Nitroaniline

(b) \( N \)-Methyl-\( p \)-nitroaniline

(c) \( N,N \)-Dimethyl-\( p \)-nitroaniline

\[
\begin{align*}
\text{Methylcyclohexane} & \quad \text{Ethylalcohol} \\
\text{Dimethyl formamide} & \\
\end{align*}
\]
FIGURE 2

Absorption Spectra of $p$-nitroaniline and its N-methylated derivatives, in EPA glass at $77^\circ$K.

________ $p$-Nitroaniline

-------- N-Methyl-$p$-nitroaniline

....... N,N-Dimethyl-$p$-nitroaniline.
appear in the published spectra relating to this work, nor is it accounted for in any accompanying σ-electron computations\textsuperscript{17,20}. The high energy \(\sim 45000\text{cm}^{-1}\) band was found to be short-axis polarized. No such data are available for the \(o\)- and \(m\)-series.

On the other hand, while Tanaka\textsuperscript{16} concludes from polarized, single-crystal absorption spectra that the \(31000\text{cm}^{-1}\) band of \(p\)-nitroaniline is indeed long-axis polarized, he also believes that this band encompasses only one electronic transition and that this transition derives from the \(^1L_a\) state of benzene (Platt's Notation). However, Tanaka's analysis may be biased in view of his association with the Nagakura-Tanaka concept of charge-transfer spectra\textsuperscript{15} which predicts one symmetric, long-axis polarized charge-transfer transition under the first absorption band of \(p\)-nitroaniline. The asymmetric intensification and skewing of the \(31000\text{cm}^{-1}\) transition of \(p\)-nitroaniline upon applying an electric field, upon increasing the solvent polarity or upon \(N\)-methylation favours the presence of two differently polarized transitions as opposed to just one long-axis polarized transition. Furthermore, the absence of these effects in \(o\)- and \(m\)-nitroanilines suggests that the lowest-energy absorption band in these isomers contains either one electronic transition or a number of similarly polarized transitions. No further assignments can be made at this point.

Several calculations are available for the electronic states of nitroanilines. Godfrey and Murrell\textsuperscript{12} , using the charge-transfer model, predict the presence of two charge transfer
transitions under the lowest energy absorption band of \( p \)-nitroaniline: one symmetric (i.e., long-axis polarized) and the other antisymmetric (i.e., short-axis polarized). Only one transition, the antisymmetric variety, is predicted to lie under the lowest-energy absorption band of \( o \)- and \( m \)-nitroaniline; the symmetric transition, in these cases is computed to lie at \( \sim 40000 \text{ cm}^{-1} \). The Godfrey-Murrell model can explain the dichroic effects in the absorption spectra and both solvent and N-methylation effects on the luminescence spectra: These perturbations affect the symmetric charge-transfer transition more than they do the antisymmetric. However, in view of the fact that the computed ground state dipole moments are found to be much smaller than the experimental values, the Godfrey-Murrell model is suspect.

The Tanaka-Nagakura calculations predict only one transition, the symmetric CT transition, to lie under the lowest-energy absorption band envelope of \( p \)-nitroaniline whereas in \( o \)- and \( m \)-nitroaniline two CT transitions are predicted, one under the lowest-energy absorption band and the other at \( 40000 \text{ cm}^{-1} \). The Tanaka-Nagakura calculation cannot account for the dichroic behaviour of the \( p \)-derivatives.

Labhart and Wagniere performed PPP-type calculations on \( p \)-nitroaniline and \( N,N \)-dimethyl-\( p \)-nitroaniline. This calculation predicts two mutually perpendicular transitions to occur under the first absorption band of \( p \)-nitroaniline but it cannot provide any account of the \( 33000 \text{ cm}^{-1} \) shoulder.
We have performed CNDO/s-CI calculation in the Del Bene-Jaffé formalism. However, these computations have not yet been analyzed.
REFERENCES


CHAPTER III

THE POLAR EXCIMER OF N,N-DIALKYL-\(\beta\)-CYANOANILINE
INTRODUCTION

During an investigation of the electronic spectroscopy of highly-polar aromatic molecules, we had occasion to study the absorption and luminescence spectroscopy of some N,N-dialkyl-p-cyanoanilines. These compounds are of particular interest for the following reasons:

Lippert, Lüder and Boos\(^1\) (LLB) have reported two luminescences for these molecules in fluid media. The two luminescences were attributed to emissive relaxations from differently-solvated excited states. This interpretation led Birks\(^2\) to a categorization of the phenomenon as a case of "dual luminescence", an attribution with which we disagree and which also discords with the original LLB model.

N,N-Dialkylanilines function as good electron donors and cyanobenzenes act as good electron acceptors in the course of formation of those types of excited state complexes which are known as\(^3,4,5\) "exciplexes". Indeed, the exciplex of donor N,N-dimethylaniline (or N,N-diethylaniline) with the acceptor cyanobenzene is well known\(^4\). In the case of N,N-dialkyl-p-cyanoaniline, where the two substituents, \(R_2N^-\) and \(-CN\), are present on the same ring skeleton, similar "exciplex formation" is to be expected but would, if it occurs, be classified as an "excimer" by virtue of the identity of the two interacting molecular species.
Chandross and Thomas have noted that N,N-dimethyl-p-cyanoaniline (NNDMPCA) exhibits three different fluorescences in methyl-cyclohexane/propionitrile solvent mixtures. They presented no details nor did they attempt any interpretation of these observations.

Cyanobenzene is known to exist in a dimeric ground state configuration in which the static dipole moments are anti-parallel. Concentration effects and excitation studies of luminescence in N,N-dialkyl-p-cyanoaniline suggest the existence of similar ground state dimer formation in this case also.

A number of widely-variant values of static dipole moment for excited NNDMPCA have been reported. The large discrepancies between different authors suggest the possibility that the various values might refer to NNDMPCA in both different excited states and in different degrees of association.

N,N-Dimethyl-p-cyanoaniline (NNDMPCA) and N,N-diethyl-p-cyanoaniline (NDEPCA) have been reported to exhibit two different fluorescences in fluid media. The ratio of intensity of these two fluorescences depends on temperature and solvent polarity. The two distinct fluorescence bands, designated "a" and "b" by LLB, were assigned, in order of increasing energy, to $^1L_a \rightarrow ^1A_1$ and $^1L_b \rightarrow ^1A_1$ electronic transitions, respectively. The solvent polarity dependence and the temperature sensitivity of the intensities of the two emissions were then interpreted as follows: In a non-polar
medium, or in a randomly-oriented polar solvent, the \(^1L_a\) state lies energetically higher than the \(^1L_b\) state, and the \(^1L_b \rightarrow ^1A_1\) fluorescence appears. In a polar solvent, the interaction with solvent molecules lowers the energy of a \(^1L_a\) state below that of the \(^1L_b\) state and a red-shifted \(^1L_a \rightarrow ^1A_1\) fluorescence results. Finally, in a weakly-polar solvent, there are two alternative lowest-energy excited states of the molecule-solvent system: The molecule in a \(^1L_b\) state surrounded by randomly distributed solvent molecules, which yields the \(^1L_b \rightarrow ^1A_1\) fluorescence; and the molecule in a \(^1L_a\) state surrounded by oriented solvent molecules which yields the \(^1L_a \rightarrow ^1A_1\) fluorescence. The relative degree of orientation of solvent dipoles with respect to the excited NNDMPCA species, and hence the ratio of the two fluorescences, should then depend on the kinetic energy of solvent molecules (i.e., on temperature) and on the solvent polarity.

We take exception to the above rationalization for the following reasons:

(i) The reported energy difference between the non-solvated \(^1L_b\) emitting state and the solvated \(^1L_a\) emitting state is \(\approx 0.8\) eV and seems rather large to be solely attributable to solvation effects. Solvates of the similarly polar molecule N,N-dimethyl-p-nitroaniline have been detected\(^1\) and can be excited on the long-wavelength edge of the lowest-energy absorption band. The luminescence is indeed red-shifted, but the shift is only 0.1 eV.

(ii) It is possible to detect the two fluorescences of types "a" & "b" in solutions of NNDMPCA in highly-polar solvents.
(e.g., ethylalcohol) where only type "a" fluorescence had been reported previously. Type "b" fluorescence of ethylalcohol solution can be induced by either dilution or acidification.

(iii) The energy of activation for the presumed $^1L_b \rightarrow ^1L_a$ inversion process, as obtained by LLB, coincides with that energy which is calculated from the dependence of solvent viscosity on temperature. This coincidence indicates that the primary affairs under consideration relate to the fluidity of the medium (i.e., to diffusion-controlled processes). Furthermore, the long-wavelength "a" fluorescence disappears on rapid freezing of the liquid solution to a glass, a phase in which both the "solvated" and the "unsolvated" ground state molecules are presumably frozen into their room-temperature caged conformations. This set of observations indicates that an excimer emission nature for the "a" fluorescence provides at least an equally viable alternative to the solvent reorganization scheme of LLB.

We have summarized our general conclusions on the luminescence characteristics of N,N-dimethyl-£-cyanoaniline in a recent publication. We present here the details of a study of the luminescence of N,N-dialkyl-£-cyanoanilines in fluid media. Our intent is a justification of the proposed excimer emission nature of the "a" luminescence.

**EXPERIMENTAL**

NNDMPCA (Aldrich Chemical Company, Inc.) and NNDEPCA (Pfaltz and Bauer, Inc.) were recrystallized a number of times from
ethylalcohol/water mixtures, the final purification step being a vacuum sublimation. All solvents were "fluorimetric grade" and were non-emissive at the level of experimental sensitivity needed in this work.

Luminescence spectra were detected, recorded and corrected using an apparatus previously described. Temperature control was achieved by standard methods. Samples were degassed by standard freeze-pump-thaw cycles and all care was taken to avoid photodecomposition. At the end of each experimental run, the total luminescence spectrum of the sample was recorded at 77°K. In all instances reported here, the spectrum so tested was found to be identical to that of the previously non-irradiated sample.

RESULTS AND DISCUSSION

NATURE OF THE LUMINESCING SPECIES:

Room-temperature fluorescence spectra of NNNDMPCA and NNDEPCA in a variety of solvents are shown in Figure 1. In non-polar methylcyclohexane, the short-wavelength "b" fluorescence (\( \sim 29000\ \text{cm}^{-1} \)) predominates. A moderate increase of solvent polarity (such as occurs, for example, in butylchloride) caused an induction of the long-wavelength "a" fluorescence (\( \sim 23750\ \text{cm}^{-1} \)). The "a" fluorescence shifts gradually to lower energies, as the solvent polarity increases, being situated at \( \sim 20900\ \text{cm}^{-1} \) in highly-polar ethylalcohol solutions where it becomes the sole emission.

In light of the items to which we have alluded in the introduction, it is our contention that the long-wavelength "a"
FIGURE 1

Representative Spectra of N,N-dialkyl-p-cyanoanilines in different solvents at 27 ± 2°C.

________ 6.4 x 10^{-4} M-NNDEPCA in methylcyclohexane.
- - - - 5 x 10^{-4} M-NNDEPCA in butylchloride.
-.--.- 1.84 x 10^{-4} M-NNDEPCA in diethylether.
-.--.- 1.47 x 10^{-5} M-NNDEPCA in ethylacetate.
....... 2.6 x 10^{-6} M-NNDEPCA in ethylalcohol.
-o-o-o- 5 x 10^{-4} M-NNDMPCA in butylchloride.
fluorescence is an "excimer" emission and that the short-wavelength "b" fluorescence is a "monomer" emission. This contention is supported by the following experimental data:

(i) The ratio of the two fluorescence intensities, \( I_a/I_b \), exhibits a concentration dependence. The \( I_b \) intensity increases upon dilution, and even becomes apparent in the highly-polar ethylalcohol solutions. Concentration effects are most obvious in slightly-polar solvents (e.g., dioxane) as shown in Figure 2 (a) and are least apparent in non-polar and highly-polar solvents because of the predominance of the "b" or "a" fluorescences, respectively, in these solvent systems.

(ii) The long-wavelength "a" fluorescence intensity of NNDMPCA in ethylalcohol solution decreases upon acidification and concomitant intensification of the short-wavelength "b" fluorescence occurs as shown in Figure 2 (b). Acidification leads to protonation of NNDMPCA, to the disappearance of the dimer absorption band (vide infra), and to a reduction in the intensity of the \( \sim 3300 \text{ cm}^{-1} \) monomer absorption band. However, the emission spectra of monomeric NNDMPCA in both ethylalcohol and acidified ethylalcohol glasses remain identical, indicating that the protonated species dissociates in the excited state and that the emitting entity, in both cases, is the unprotonated NNDMPCA. We interpret these observations by assuming that protonation merely decreases the number of ground-state unprotonated NNDMPCA molecules available for excimer trapping of the excited unprotonated NNDMPCA species.

(iii) The long-wavelength fluorescence of NNDEPCA (or NNDMPCA) in
FIGURE 2

(a) Fluorescence spectra of NNDMPCA in dioxane at 27 ± 2°C. The two spectra are normalized to a common intensity at 410μm. The fluorescence of the monomer in the concentrated solution is distorted by inner-filter effects.

- - - - 2.2 x 10^-4 M-NNDMPCA
- - - - 8.8 x 10^-6 M-NNDMPCA

(b) Effect of protonation on NNDMPCA fluorescence at 27 ± 2°C.

- - - - 2 x 10^-4 M-NNDMPCA in ethylalcohol.
- - - - 2 x 10^-4 M-NNDMPCA in acidified ethylalcohol (5% HCl.).

(c) Quenching of NNDEPCA fluorescence by addition of N,N-Dimethyl-p-nitroaniline at 27 ± 2°C.

- - - - 2.1 x 10^-6 M-NNDEPCA in ethylalcohol.
- - - - a mixture of 4.96 x 10^-5 M-NNDEPCA and 1.03 x 10^-5 M N,N-dimethyl-p-nitroaniline in ethylalcohol.
ethylalcohol is quenched on adding a non-fluorescent highly-polar nitro compound of dipole moment comparable to that of NNDMPCA and of similar geometry. Such an effect is shown in Figure 2 (c). The absorption spectrum of the mixture and the total emission of the glassy solution at 77°K are identical to the respective sums of absorption spectra and of emission spectra of the separate components. The lifetime of NNDMPGA monomer and dimer emissions are unaffected by the added nitrocompound, indicating also that no ground state interactions of significance occur between NNDMPCA and N,N-dimethyl-p-nitroaniline. Thus, we interpret the quenching of the "a" fluorescence by assuming that N,N-dimethyl-p-nitroaniline competes with ground-state NNDMPCA molecules for trapping of excited NNDMPCA molecules as non-fluorescent "hetero-excimers".

Thus, the assignment of the long-wavelength "a" fluorescence of N,N-dialkyl-p-cyanoanilines as an excimer fluorescence acquires some justification. Certainly, it is considerably more difficult to justify observations (i) - (iii) on the basis of a solvent reorientation scheme.

The two fluorescences denoted "a" and "b" possess the same excitation spectrum and this spectrum replicates the monomer absorption spectrum. Absorption spectral studies, however, also reveal the existence of a weak long-wavelength absorption band in the 30000 - 26000 cm⁻¹ region, an absorption which has been assigned to (NNDMPCA)₂ dimers. Excitation in this band leads to a third, distinctly-different emission which maximizes in the region


26000 - 25000 cm\(^{-1}\) and produces none of the monomer or excimer emissions. These results are shown in Figure 3. The excitation spectrum of this dimer emission is different from that of the monomer or excimer and encompasses both the monomer and dimer absorption peaks. In sum, then, the fluorescence spectrum of N,N-dialkyl-\(p\)-cyanoanilines at room temperature may contain three fluorescence bands which, in order of decreasing energy correspond to "monomer", "dimer" and "excimer" emissions, respectively.

**KINETIC SCHEME:**

We suppose that those kinetic events applicable for non-polar excimers also occur for highly-polar excimers. These steps are listed in Table 1. No triplet state species are considered because of the invariance of our experimental results to aeration or deoxygenation. Nor do we consider any dimer-excimer interconversion events because of the mutual exclusivity of their respective excitation spectra.

In a steady state approximation, we may write the ratio of excimer to monomer fluorescence intensities (previously denoted \(I_a/I_b\)) as:

\[
\frac{I_{FE}}{I_{FM}} = \frac{k_{FE}}{k_{FM}} \left( \frac{k_{EM}[M_0]}{k_E + k_{ME}} \right)
\]

**TEMPERATURE DEPENDENCE OF FLUORESCENCE INTENSITIES:**

The temperature dependence of \(I_{FE}/I_{FM}\) is qualitatively identical but quantitatively different in solvents of different polarities and can be summarized as:
FIGURE 3
Absorption and fluorescence spectra of NNDEPCA in ethylalcohol at 27 ± 2°C.

Absorption spectrum of 5.25 x 10^{-5}M-solution in a 0.5cm path length.

Fluorescence of a 2.1 x 10^{-6}M-solution excited at 300μm.

Fluorescence of a 2.1 x 10^{-6}M-solution excited at 345μm.
In slightly polar solvents (e.g., diethylether and butyl-chloride), \( \frac{I_{FE}}{I_{FM}} \) increases with decreasing temperature, reaches a maximum, and then decreases as shown in Figures 4 (a&b). The temperature at which \( \frac{I_{FE}}{I_{FM}} \) is a maximum, \( T_m \), is higher the larger the polarity of either the solvent or the solute.

In highly polar solvents (e.g., ethylalcohol) only the descending part of the curve is obtained in the temperature range studied here. It is presumed that \( T_m \) lies above room temperature in these instances. A typical result is shown in Figure 4 (c).

In non-polar methylcyclohexane, no excimer fluorescence is observed in the same concentration and temperature range which was used in the study of other solvent systems. The monomer fluorescence in this solvent intensifies with decreasing temperature, presumably because of a decrease in quenching efficiency or an increase in concentration (i.e., volume shrinkage).

In order to interpret the temperature dependence of \( \frac{I_{FE}}{I_{FM}} \), we may rewrite Eq. 1 as:

\[
\frac{I_{FE}}{I_{FM}} = \frac{k_{FE}^o e^{-\Delta E_{EM}/RT}}{k_{FM} (k_{FE} + k_{QE} e^{-\Delta E_{QE}/RT} + k_{ME} e^{-\Delta E_{ME}/RT})} \ldots \ldots 2
\]

where we assume that, as is the case for non-polar excimers of aromatic hydrocarbons\(^{16}\), \( k_{FE} \) and \( k_{FM} \) are independent of temperature.

Plots of \( \log \frac{I_{FE}}{I_{FM}} \) vs. 1/T are shown in Fig. 5. The log \( \frac{I_{FE}}{I_{FM}} \) vs. 1/T functional dependence, and the deductions based upon it, may now be summarized:
FIGURE 4

Temperature dependence of $I_{FE}/I_{FM}$ for N,N-dialkyl-$p$-cyanoanilines in different solvents:

(a) in Diethylether

(b) in Butylchloride

(c) in Ethylalcohol

-------- NNDMPCA solute

________ NNDEPCA solute

Arrows refer curves to the appropriate scale.
FIGURE 5

Plot of $\log \frac{I_{FE}}{I_{FM}}$ vs. $1/T$ in different solvents:

(a) In Diethlyether

(b) in Butylchloride

(c) in Ethylalcohol

________ NNDMPCA solute

- - - - NNDEPCA solute

Arrows refer curves to the appropriate scale.
(i) In an ethylalcohol solvent, a linearity of negative slope is obtained, indicating the predominance of the temperature sensitivity located in the numerator (i.e., \( k_{FE} \gg k_{QE} + k_{ME} \)). The values of \( \Delta E_{EM} \) thus obtained are in good agreement with \( \Delta E_\eta \), the energy of activation obtained from plots of \( \log \eta_\eta / \eta_\eta \) vs. \( 1/T \) where \( \eta \) is the solvent viscosity. Values of \( \Delta E_{EM} \) and \( \Delta E_\eta \) are tabulated in Table 2.

(ii) For diethylether and butylchloride solutions, the plots of \( \log I_{FE}/I_{FM} \) vs. \( 1/T \) are qualitatively identical to those obtained for pyrene excimers\(^{17}\). At temperatures higher than \( T_m \), the limiting slope is positive, indicating the predominance of some one of the temperature dependent terms in the denominator (i.e., \( k_{QE} \gg k_{FE} + k_{ME} \) or \( k_{ME} \gg k_{FE} + k_{QE} \)). At temperatures lower than \( T_m \), the limiting slope is negative, indicating the predominance of the term in the numerator. Thus, the limiting slopes provide values of \( \Delta E_{EM} \) which, as is evident from Table 2, are in good agreement with \( \Delta E_\eta \).

(iii) The good correspondence between the different values of \( \Delta E_{EM} \) and \( \Delta E_\eta \) suggests that excimer formation in \( N,N\)-disalkyl-\( p \)-cyanoanilines is a diffusion controlled process. The value obtained by LLB for the activation energy associated with a presumed \( ^1L_a \leftrightarrow ^1L_b \) inversion process was 3.6 kcal/mole, in somewhat poorer agreement with \( \Delta E_\eta \) than that computed here on the basis of an excimer model. The LLB model attributed the activation energy to the shifting of single solvent molecules relative to each other in the relaxation process which supposedly led to the lower-energy solvated "a" state.

(iv) Birks et al.\(^{16}\) have suggested that \( k_{ME} \gg k_{FE} + k_{QE} \) for excimers
of polycyclic aromatic hydrocarbons. Assuming the same inequality to hold for excimers of N,N-dialkyl-p-cyanoanilines, the slope of the high temperature part of log \( \frac{I_{FE}}{I_{FM}} \) vs. \( \frac{1}{T} \) plot yields \( \Delta E_{ME} - \Delta E_{EM} \), which is the excimer binding energy, \( B \). Values of \( B \) calculated in this manner are tabulated in Table 2 and appear to be insensitive to either solvent polarity or solvent viscosity. Binding energies of excimers of aromatic hydrocarbons exhibit a similar insensitivity to the nature of the solvent\(^{16}\).

(v) Assuming that \( k_{ME} \gg k_{QE} \) and that \( k_{FE} \) and \( k_{FM} \) are independent of \( T \), we can rewrite Eq. 2 as:

\[
\frac{I_{FE}}{I_{FM}} = \frac{k_{FE}^0 e^{-\Delta E_{EM}/RT}}{k_{FM}^0 e^{-\Delta E_{ME}/RT}} \left[ I_{M0} \right] \quad ...... 3
\]

At \( T_m \), where

\[
\frac{\partial}{\partial T} \left( \frac{I_{FE}}{I_{FM}} \right) = 0
\]

we find

\[
\frac{\Delta E_{ME}}{\Delta E_{EM}} = 1 + \left( \frac{k_{FE}}{k_{FM}} \right) \quad ...... 4
\]

Thus, \( \Delta E_{ME} \) is given by the sum of the activation energies obtained from the low and high temperature limiting slopes. The values of \( \left( \frac{k_{FE}}{k_{FM}} \right) \) which are given in Table 2 indicate a greater dependence on the nature of the solvent than on that of the solute.

**SOLVENT EFFECTS:**

The nature of the solvent has a profound effect on the energy and
<table>
<thead>
<tr>
<th>Solvent</th>
<th>Solvent properties</th>
<th>NNDMPGA</th>
<th>NNDEPCA</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>η&lt;sup&gt;(a)&lt;/sup&gt;</td>
<td>ε&lt;sup&gt;(a)&lt;/sup&gt;</td>
<td>Δε&lt;sup&gt;(b)&lt;/sup&gt;</td>
</tr>
<tr>
<td>Diethylether</td>
<td>0.2</td>
<td>4.3</td>
<td>1.98</td>
</tr>
<tr>
<td>(T)</td>
<td>(20&lt;sup&gt;°&lt;/sup&gt;C)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Butylchloride</td>
<td>0.405</td>
<td>7.3</td>
<td>2.0&lt;sup&gt;(c)&lt;/sup&gt;</td>
</tr>
<tr>
<td>(T)</td>
<td>(30&lt;sup&gt;°&lt;/sup&gt;C)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ethylalcohol</td>
<td>1.078</td>
<td>24.55</td>
<td>3.01</td>
</tr>
<tr>
<td>(T)</td>
<td>(25&lt;sup&gt;°&lt;/sup&gt;C)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
a) Taken from ref. 19; $\eta$ is the viscosity in centipoise and $\varepsilon$ is the dielectric constant.

b) Calculated from $\log \eta$ vs. $1/T$ plots using $\eta$ values at different temperatures as tabulated in: "Handbook of Chemistry and Physics" (R.C. Weast, ed.), The Chemical Rubber Company, Cleveland, Ohio, 52nd edition, 1971.

c) Calculated from the values of $\eta$ at 15 and 30°C as cited in footnote a.

d) The temperature ($^\circ K$) at which $L_{FE}/L_{FM}$ is a maximum.

e) Activation energy (kcal/m) calculated from the slope of the low temperature portion of $\log L_{FE}/L_{FM}$ vs. $1/T$ plots.

f) Excimer binding energy (kcal/m) calculated from the slope of the high temperature portion of $\log L_{FE}/L_{FM}$ vs. $1/T$ plots.

g) Data for the high temperature portion of the range were not determinable.

h) The value of $k_{FE}/k_{FM}$ at $T_m$. 
emissivity of highly-polar N,N-dialkyl-p-cyananiline excimer:

-----The energy of excimer luminescence is very sensitive to solvent polarity. LLB report a linear decrease of the frequency of the long-wavelength fluorescence as a function of increasing

\[ \Delta f = \frac{D-1}{2D+1} \cdot \frac{n^2 - 2}{2n^2 + 1} \]

Since \( \Delta f \) is a fairly good measure of the orientation polarization of the solvent\(^{17}\), and since the frequency decrease is very sharp, it follows that the excimer is not only polar but that an actual increase of dipole moment is occasioned by the act of excimer formation\(^{18}\).

-----The intensity of excimer luminescence depends on solvent viscosity. The solvent viscosity alters those rate constants, such as \( k_{EM} \) and \( k_{QM} \), which are diffusion controlled. As a result, the ratio \( \frac{I_{FE}}{I_{FM}} \) for NNDMPCA in two solvents of different viscosities and similar polarities decreases considerably as the viscosity increases. Such an effect is shown in Table 3 for solutions in ethylalcohol and propylene glycol.

-----Solvent polarity also affects the intensity ratio \( \frac{I_{FE}}{I_{FM}} \). As shown in Table 3 for two solvents of different polarities and similar viscosities, methylcyclohexane and ethylalcohol, \( \frac{I_{FE}}{I_{FM}} \) exhibits a significant increase in the solvent of larger polarity.

-----Specific solvent-solute and solvent-solvent interactions also appear to alter the ratio \( \frac{I_{FE}}{I_{FM}} \). LLB found that a plot of log \( \frac{I_{FE}}{I_{FM}} \) vs. \( \Delta f \) was linear, if one allowed for a considerable scatter of the experimental data. A replot of their data is given in
Figure 6, wherein it is seen that two linearities, each representative of a family of solvents of similar chemical structure, are generated. Thus, while orientation polarization effects due to the solvent are unquestionably important, we must also conclude that specific solvent-solute interactions, which are related to the chemical structure of the two solvent series, are not without significance. Indeed, one might go further and assert that alcoholic solvents, all of which cluster in a small region of the $\log \frac{I_{PE}}{I_{FM}}$ vs. $\Delta f$ plot, represent an instance in which specific solvent-solute and solvent-solvent interaction (e.g., hydrogen bonding) might very well be larger than interactions of dipole-dipole type. In the same vein, it is also noteworthy that the correspondence of $\Delta E_{EM}$ and $\Delta E_{\eta}$ in ethylalcohol solution is rather poor compared to that in other solvents, again denoting the possible importance of specific intermolecular "chemical" interactions.

The nature of the solvent may also affect the radiative rate constants. We have no fluorescence lifetime data available and, consequently, we cannot be specific on the effect of solvent on the rate constants $k_{PE}$ and $k_{FM}$ for NNDMPGA. The available data for non-polar pyrene excimers would suggest, however, that $k_{PE}$ is independent of either solvent polarity or viscosity; on the other hand, $k_{FM}$ for polar naphthylamines and 5-dimethylaminonaphthalene-1-sulphonamide does decrease as the solvent polarity increases. This latter, if also transferable to $k_{PE}$, may well be an important factor for the luminescence characteristics of polar excimers.
Plot of $\log \frac{I_{FE}}{I_{FM}}$ vs. $\Delta f$ (from data of LLB). Points are identified as follows:

1), Dioxane; 2), Tetrahydrofuran; 3), Butylether; 4), Acetic anhydride; 5), Benzylacetate; 6), Ethylacetate; 7), Diethylether; 8), $\text{iso}$Propanol; 9), Ethanol; 10), Cyclohexanol; 11), n-Propanol; 12), Tetrachloroethane; 13), o-Dichlorobenzene; 14), Bromobenzene; 15), Tri-fluorotoluene; and 16) Chlorobenzene.

Alcohols are identified by circles; ethers, esters and anhydrides are identified by squares; and halides are identified by triangles.
### TABLE 3
Solvent Dependence of the Excimer/Monomer Fluorescence Intensity Ratio At Room Temperature

<table>
<thead>
<tr>
<th>Solvent</th>
<th>η(a)</th>
<th>ε(a)</th>
<th>I&lt;sub&gt;FE&lt;/sub&gt;/I&lt;sub&gt;FM&lt;/sub&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>NNDMPCA</td>
</tr>
<tr>
<td>Diethylether</td>
<td>0.233(b)</td>
<td>4.335(b)</td>
<td>0.1</td>
</tr>
<tr>
<td>Butylchloride</td>
<td>0.405(c)</td>
<td>7.39(b)</td>
<td>0.6</td>
</tr>
<tr>
<td>Ethylalcohol</td>
<td>1.078(d)</td>
<td>24.55(d)</td>
<td>13.5</td>
</tr>
<tr>
<td>Methylcyclohexane</td>
<td>0.734(b)</td>
<td>2.07(b)</td>
<td>0</td>
</tr>
<tr>
<td>Propylene glycol</td>
<td>56.0(b)</td>
<td>3.2(b)</td>
<td>3.6</td>
</tr>
<tr>
<td>Ethylacetate</td>
<td>0.441(d)</td>
<td>6.02(d)</td>
<td>5.2(f)</td>
</tr>
<tr>
<td></td>
<td>0.455(b)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

- a) η is viscosity in centipoise and ε is the dielectric constant; taken from ref. 19.
- b) at 20°C
- c) at 30°C
- d) at 25°C
- e) A 2x10<sup>-6</sup> M-solution was used in order to retain I<sub>FM</sub> and I<sub>FE</sub> on scale. For concentration in the range 10<sup>-4</sup> - 10<sup>-5</sup>M, we find 90 ≤ I<sub>FE</sub>/I<sub>FM</sub> ≤ 100.
- f) From LLB, for a 10<sup>-4</sup> M-solution.
We now emphasize that the intensification of the excimer fluorescence intensity of NNMPCA (or NNDEPCA) which occurs in polar solvents is contrary to the behaviour observed for highly-polar exciplexes where an opposite effect is readily observed.\(^{23,24}\)

The quenching of exciplex fluorescence which occurs in polar solvents has been attributed to the formation of non-fluorescent solvated ion-pairs, the existence of which is assured by the detection of the transient $S_n \rightarrow S_1$ absorption spectra\(^{25}\) of the ionic species. A similar quenching has been observed for intramolecular exciplexes in polar solvents.\(^{6,26}\) However, the quenching of the exciplex fluorescence intensity which occurs in polar solvents becomes less apparent as the charge-transfer character of the exciplex becomes smaller\(^{27}\) (i.e., as the exciplex approaches the case of a hetero-excimer). Thus, the importance of ion-pair formation in quenching might appear to be inapplicable in the case of a true excimer where one might expect charge resonance but no charge transfer. In this sense, the non-quenching of excimer fluorescence in polar solvents need not be construed as anomalous.

We interpret the intensification of $I_{FE}$ for NNMPCA in polar solvents in one or both of two ways. Firstly, an increase of the lifetime of $^{1}M^*$ species in polar solvents, as observed for 5-dimethylaminonaphthalene-1-sulphonamide would lead to a larger number of collisions of $^{1}M^*$ and $^{1}M_0$ species and, hence, to a higher probability of excimer formation. Secondly, solvent-solute and solvent-solvent specific interactions and dipole-dipole interactions
may lead to a modicum of long-range order in the solute-solvent system. If such an ordering produced an arrangement of transition dipoles suitable to excimer formation, it might be expected to have a large affect on the probability of formation of a highly-polar excimer. Such an effect has been posited in the formation of non-polar excimers.

**GEOMETRY AND DIPOLE MOMENT OF EXCIMERS:**

The mutual exclusivity of the dimer and excimer excitation spectra suggests that they are geometrically dissimilar and that they are not readily interconvertible within the lifetime of any of the excited singlet states. If the dimer possesses an anti-parallel dipole configuration, it follows that this sort of geometric grouping does not apply for the excimer. Furthermore, since the static dipole moment of the excimer is assuredly larger than that of either of its components, whether they be in $^1S_0$, $^1L_a$ or $^1L_b$ states, it follows that a parallel (or nearly parallel) dipole configuration represents a good initial approximation to the excimer geometry.

The subject of static dipole moments for the various states of NNDMPCA is quite confusing. That of the $^1S_0$ state is 6.6D. That of the state which emits the "a" (or "excimer") fluorescence, as determined by LLB from standard Stokes shifts vs. $\Delta f$ arguments, is 23D. That of the $^1S_1$ state, which emits the "b" (or monomer, or $^1L_b \rightarrow ^1S_0$) luminescence, as determined by us from Stokes shifts vs. $\Delta f$ arguments, is 18D. This last value, in
particular, appears to be much too large. The $^{1}L_{b} \rightarrow ^{1}S_{0}$ transition is short-axis polarized and it is difficult to see how it might produce any significant charge separation along the long-axis of the molecule. If this argument be correct, one then might expect the dipole moment of the $^{1}L_{b}$ state to be not much larger than 6.6D. If so, one must immediately conclude that the Stokes shift approach leads to a gross over-estimation of $\mu$ - values or that $\mu$ is largely solvent-determined. In any event, granting comparable over-estimation for the two $\mu$ - values associable with the luminescing states, one notes that $6.6 + 18 = 24.6$D and that the closeness of this number to 23D provides support for the idea that the excimer consists of a $^{1}L_{b}$ and a $^{1}S_{0}$ molecule arranged in a parallel dipole configuration. Nonetheless, in view of all the other conflicting dipole moment data which exists for NNDMPCA, we must conclude that the above arguments are quite specious.

CONCLUSIONS

The conclusions of this work are:

1. The concentration dependence of the luminescence intensity, and the effects of external quenchers on it, suggest that the long-wavelength fluorescence of N,N-dialkyl-p-cyanoanilines can be assigned as an excimer fluorescence.

2. Solutions of N,N-dialkyl-p-cyanoanilines exhibit three fluorescence spectra. These correspond, in order of increasing energy, to monomer, dimer and excimer luminescences, respectively. The luminescence of crystalline NNDMPCA is solely that of the dimer.
REFERENCES


15. See ref. 2, p. 432 ff.


28. Hetero-excimers are exciplexes in which the two components possess almost similar \( \pi \)- electronic energy levels, ionization potentials and electron affinities. The cases of naphthalene-cyanonaphthalene and aromatic hydrocarbon-alkylated aromatic
hydrocarbon provide examples. (See Ref. 2, p. 420).


30. A value of 12.5D has been quoted by Labhart\(^\text{31}\) for the terminal state of the lowest-energy absorption process in NNDMPCA. The nature of Labharts' electrodichroic absorption measurements restricts their utility to intense absorption regions; hence, we infer that \(\mu = 12.5\)D refers to a \(1_L_a\) state of NNDMPCA. Granted this attribution, and the near certainty that \(\mu(1_L_a) > \mu(1_L_b)\), it follows that the arguments of the previous paragraph apply equally to a situation where the excimer consists of a \(1_L_a\) and \(1_S_0\) molecule arranged in a parallel dipole configuration. Finally, Czekalla, Liptay and Meyer\(^\text{32}\) quote a value \(11 \leq \mu \leq 14.5\)D, as determined from luminescence dichroism, for the "a" state of NNDMPCA. This number is possibly compatible with a parallel dipole configuration of \(1_S_0\) (6.6D) and \(1_L_b\) (\(\sim 6.6\)D) molecules but not with a similar configuration of \(1_S_0\) (6.6D) and \(1_L_a\) (12.5D) molecules. It is, however, compatible with a perpendicular dipole arrangement involving the \(1_S_0\) and \(1_L_a\) states.


CHAPTER IV

A SELF-COMPLEX OF N,N-DIALKYL-p-CYANOANILINES
INTRODUCTION

The total luminescence spectrum of solutions of N,N-dialkyl-p-cyanoanilines may consist of five different emissive events: Two phosphorescences and three fluorescences. The longest wavelength fluorescence has been described in some detail and has been assigned to an excimer luminescence. The fluorescence and phosphorescence of shortest wavelengths refer to monomer emission events of probable \( 1L^0 \rightarrow 1S_0 \) and \( 3L_a \rightarrow 1S_0 \) types, respectively. It is the contention of this paper that the fluorescence of intermediate wavelength and the phosphorescence of longest wavelength represent the emissive output of a self-complex which we will, henceforth, refer to as a dimer, and which, unlike the excimer, is stable when the monomer components of the self-complex are in their \( 1S_0 \) ground states.

All experimental techniques used here have been described previously and will not be discussed further.

RESULTS

ABSORPTION SPECTRA

The long-wavelength absorption spectra of N,N-dimethyl-p-cyanoaniline (NNDMPCA) and N,N-diethyl-p-cyanoaniline (NNDEPCA) are shown in Fig. 1. The spectrum contains two distinct absorption features: An intense band in the region \( 33000 \leq \nu \leq 34500 \text{ cm}^{-1} \) with \( \epsilon = 2 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1} \); and a weak band of much lower absorptivity in the region \( 29000 \leq \nu \leq 31000 \text{ cm}^{-1} \).
Absorption spectra of (a), NNDMPCA and (b), NNDEPCA at 25°C.

----- In methylcyclohexane

-------- In ethylalcohol
The intensity of this weak band is \( \sim 10^2 \) times less than that of the 33000 cm\(^{-1}\) band and is quite sensitive to solvent polarity, being larger in polar solvents and almost absent in non-polar media. The intensity of the weak band is also sensitive to temperature and is, for example, readily detectable in hydrocarbon glasses at 77^\circ\text{K}. It is this weak band which we assign to the \(^1\text{S}_1 \rightarrow \text{^1S}_0\) absorption event in the dimer.

The intense band encompasses at least two distinct absorptive events of the monomer. These two events, in a non-polar environment and in order of increasing energy, are thought\(^{5-7}\) to be \(^1\text{L}_b \rightarrow \text{^1S}_0\) and \(^1\text{L}_a \rightarrow \text{^1S}_0\) excitations. Since the \(^1\text{L}_a\) state possesses a significant charge transfer characteristic and is highly polar, it is also thought\(^{5-7}\) that these two states, \(^1\text{L}_a\) & \(^1\text{L}_b\), can interchange their relative energy positions and that, in highly-polar solvents, the \(^1\text{L}_a \rightarrow \text{^1S}_0\) can be of lower energy than the \(^1\text{L}_b \rightarrow \text{^1S}_0\) transition. Indeed, that emission now identified\(^2\) as an excimer fluorescence was previously assigned\(^{5-7}\) to a \(^1\text{L}_a \rightarrow \text{^1S}_0\) process of a highly-solvated NNDMPGA monomer.

In slightly acid media, the \( \sim 29000\text{cm}^{-1}\) band dissappears and the intensity of the \( \sim 33000\text{cm}^{-1}\) band decreases. These effects are exactly reversible upon neutralization with NH\(_4\)OH solutions and may be regenerated, at will, as long as the acidity remains low. Such effects are shown in Fig. 2. The decrease of intensity in the \( \sim 33000\text{cm}^{-1}\) band is readily rationalized\(^8\): Protonation of the amino group leads to a decrease of the charge transfer characteristic of
FIGURE 2

Room temperature absorption spectra of NNMDPCA in neutral and acid media.

_____ Ethylalcohol

------ Ethylalcohol, 1% hydrochloric acid.

....... Ethylalcohol, 5% hydrochloric acid.

Sets (a) and (b) refer to 0.1 and 1cm cells, respectively.
the $^1L_a + ^1S_0$ monomeric event and removes this transition to a new energy location. The disappearance of the $\sim 29000\text{cm}^{-1}$ band, however, is not readily explicable along such lines. It is also well to emphasize that the reversibility which pertains to weakly acid media does not hold at higher acid strengths: Chemical reaction of an irreversible sort sets in at high pH.

Neither the $\sim 33000$ nor the $\sim 29000\text{cm}^{-1}$ bands obey the Beer-Lambert law: The former intensifies and the latter weakens as the concentration of the absorber decreases. Such effects are shown in Fig. 3. It is suggested, therefore, that the $\sim 29000\text{cm}^{-1}$ band refers to some sort of solute-solute association (or self-complex) and that only the $\sim 33000\text{cm}^{-1}$ band refers to a truly monomeric absorption event. The possibility of association, indeed, is not very surprising: It is known$^{9-12}$ that organic nitriles exist as dimers in the liquid state; it is known$^{13}$ that cyanobenzene forms dipole-dipole dimers in which the dipole orientations are anti-parallel; and it is only to be expected that the similar (and considerably more-polar) $N,N$-dialkyl-$\pi$-cyanoanilines would do likewise.

If we assume a dimer stoichiometry, we can determine a formation constant, $K$. The optical density of the $\sim 33000\text{cm}^{-1}$ band is

$$D = \varepsilon c \lambda(1-\alpha)$$

where $\varepsilon$ & $c$ are monomer extinction and concentration, respectively; where $\lambda$ is path length; and $\alpha$ is the degree of association. A
FIGURE 3

Effect of concentration on room temperature absorption spectra of 
NNDMPGA in different solvents.

(a) ....... $5.97 \times 10^{-4}$M, 0.1cm cell.
    _______ $2.97 \times 10^{-4}$M, 0.1cm cell.
    -------- $1.19 \times 10^{-5}$M, 2.5cm cell.
In an ethylacetate solvent.

(b) ....... $8.36 \times 10^{-4}$M, 0.1cm cell.
    _______ $3.34 \times 10^{-4}$M, 0.1cm cell.
    -------- $1.34 \times 10^{-5}$M, 2.5cm cell.
In a p-dioxane solvent.
monomer-dimer equilibrium leads to

\[ D = \varepsilon c l - D^2 K / \varepsilon l \]

Hence, if the absorption spectra of two solutions of different \( c \) but constant \( \varepsilon l \) are obtained, it follows that

\[ \Delta D = D_1 - D_2 = (D_2^2 / \varepsilon_2 - D_1^2 / \varepsilon_1) K / \varepsilon \]

Since \( \varepsilon \) may be determined for a very dilute solution, it follows that \( K \) is obtainable. Data so processed are shown in Table 1. Given the supposition of a dimer stoichiometry, it follows that \( K = 10^2 \times \text{m} \). It also follows that \( K \) is smaller (and, hence, the extinction coefficient of the 29000 cm\(^{-1}\) dimer band is larger) in polar media. The data of Table 2 for NNDMPCA are parallel in most regards to those for NNDEPCA except that \( K \) for the latter solute is somewhat smaller.

Considerable resolution is exemplified in organic glasses at 77°K and is illustrated in Fig. 4. These spectra are remarkable for two reasons:

- The spectrum can be resolved into two distinct vibronic progressions, I & II of Table 2, each with an average interval of \( \sim 1750 \text{ cm}^{-1} \). Since the \( \text{C} = \text{N} \) stretching frequency of the \( ^1S_0 \) state lies at 2230 cm\(^{-1}\) in NNDMPCA, since the symmetric ring-breathing vibration lies at \( \sim 1600 \text{ cm}^{-1} \), and since our own Raman and IR data indicate a complete absence of vibrational frequencies in the 1600 - 2200 cm\(^{-1}\) range for both the crystal and solutions of NNDEPCA, we feel confident that the \( \sim 1750 \text{ cm}^{-1} \) frequency represents a \( \text{C} = \text{N} \) stretching mode in the excited state(s).
FIGURE 4

Absorption spectra of NNDEPCA in 3-methylpentane.

........ 2.3x10⁻⁵M, 0.5cm cell at 25°C.

________ Same solution, 0.4cm cell at 77°C.

-.--.- 1.15x10⁻⁴M, 0.5cm cell at 25°C.

------- Same solution, 0.4cm cell at 77°C.
<table>
<thead>
<tr>
<th>Solvent</th>
<th>c (m/(\ell))</th>
<th>(a) (cm)</th>
<th>(e f^h) (x10(^{-5}))</th>
<th>D</th>
<th>(\Delta D) (x10(^{-3}))</th>
<th>(K/e) (x10(^{-4}))</th>
<th>(K^c) (x10(^{-2}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dioxane</td>
<td>3.34x10(^{-4})</td>
<td>0.1</td>
<td>0.86</td>
<td></td>
<td>3.34</td>
<td>0.035</td>
<td>4.9</td>
</tr>
<tr>
<td></td>
<td>1.34x10(^{-5})</td>
<td>2.5</td>
<td>0.90</td>
<td></td>
<td>2.69(^d)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ethylacetate</td>
<td>2.99x10(^{-4})</td>
<td>0.1</td>
<td>0.79</td>
<td></td>
<td>2.99</td>
<td>0.03</td>
<td>5</td>
</tr>
<tr>
<td></td>
<td>1.2 x10(^{-5})</td>
<td>2.5</td>
<td>0.82</td>
<td></td>
<td>2.74(^d)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Acetonitrile</td>
<td>2.84x10(^{-4})</td>
<td>0.1</td>
<td>0.73</td>
<td></td>
<td>2.84</td>
<td>0.012</td>
<td>2.3</td>
</tr>
<tr>
<td></td>
<td>1.14x10(^{-5})</td>
<td>2.5</td>
<td>0.74</td>
<td></td>
<td>2.61(^d)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dimethyl-formamide</td>
<td>2.96x10(^{-4})</td>
<td>0.1</td>
<td>0.73</td>
<td></td>
<td>2.96</td>
<td>0.015</td>
<td>3</td>
</tr>
<tr>
<td></td>
<td>1.18x10(^{-5})</td>
<td>2.5</td>
<td>0.75</td>
<td></td>
<td>2.54(^d)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
a) Optical path in cm.

b) Molar extinction coefficient in \( \text{M} \text{cm}^{-1} \).

c) Equilibrium constant in \( \text{M} \text{cm}^{-1} \).

d) Molar extinction coefficient for the solution of lower concentration, in which it is assumed that dimer concentration is minimal.
The intensity of the longer-wavelength progression II increases considerably relative to progression I as the concentration of the glassy solution increases. Unfortunately, experiments such as these are rather difficult to do and, as a result, we can only infer that progression I refers to monomer and progression II to a self-complex. This inference is clearly substantiated by reference to Fig's. 1, 2 & 3.

The ~29000 cm$^{-1}$ band is clearly of solute-solute association origins. This statement is borne out by non-Beer's law behavior, by studies in low-temperature hydrocarbon glasses where solute-solvent interactions are surely small and, to some degree, by the study of weakly-acid solutions. That the solute-solute interactions lead to a dimer stoichiometry is borne out, somewhat weakly to be sure, by the data of Table 1 and, somewhat more strongly, by the fact that the absorption of the associate exhibits a fair degree of vibronic resolution (Progression II of Table 2). The monomer progression (Progression I of Table 2) probably refers to a $^{1}L_a \rightarrow ^{1}S_0$ transition. This conclusion is based on a correlative study of substituted benzonitriles and, if correct for N,N-dialkyl-p-cyanoanilines, forces us to conclude that the $^{1}L_a \& ^{1}L_b$ states of these latter molecules are heavily mixed by vibronic interactions. This, in view of the energetic proximity of the $^{1}L_a \& ^{1}L_b$ states, is certainly possible and is the only way we can rationalize the occurrence of a dominant C=N stretching frequency in a $^{1}L_b \rightarrow ^{1}S_0$ transition.

**LUMINESCENCE SPECTRA**

The low-temperature luminescence spectra of glassy solutions
### Table 2

**Vibrational Analysis of the Absorption Spectra of Figure 4**

<table>
<thead>
<tr>
<th>Progression I</th>
<th></th>
<th></th>
<th>Progression II</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>( \tilde{\nu} )</td>
<td>( \Delta\tilde{\nu} )</td>
<td>( \Delta\tilde{\nu}/n )</td>
<td>( \tilde{\nu} )</td>
<td>( \Delta\tilde{\nu} )</td>
<td>( \Delta\tilde{\nu}/n )</td>
</tr>
<tr>
<td>(cm(^{-1}))</td>
<td>(cm(^{-1}))</td>
<td>(cm(^{-1}))</td>
<td>(cm(^{-1}))</td>
<td>(cm(^{-1}))</td>
<td>(cm(^{-1}))</td>
</tr>
<tr>
<td>29630</td>
<td>0.0</td>
<td></td>
<td>28777</td>
<td>0.0</td>
<td>0.00</td>
</tr>
<tr>
<td>31056</td>
<td>1426</td>
<td>1426</td>
<td>30534</td>
<td>1757</td>
<td>1757</td>
</tr>
<tr>
<td>33333</td>
<td>3703</td>
<td>1851</td>
<td>32258</td>
<td>3481</td>
<td>1740</td>
</tr>
<tr>
<td>34843</td>
<td>5211</td>
<td>1737</td>
<td>34014</td>
<td>5237</td>
<td>1745</td>
</tr>
</tbody>
</table>

Average = 1723

Average = 1745
are shown in Fig. 5. Excitation in the monomer absorption region yields the fluorescence and phosphorescence of Fig. 5(b). The phosphorescence is of relatively long lifetime, $\tau_p \approx 2$ sec and the fluorescence is essentially identical to that observed under similar excitation conditions in fluid solutions at 25°C. Excitation in the dimer absorption region yields the two new fluorescence and phosphorescence emissions of Fig. 5(a). The phosphorescence is of intermediate lifetime, $\tau_p \approx 0.5$ sec, and the fluorescence is essentially identical to that observed under similar excitation conditions in fluid solutions at 25°C which exhibit absorptivity at $\sim 29000 \text{cm}^{-1}$.

The luminescence of a crystal of NNDMPCA and NNDEPCA consists solely of dimer emission, none or negligible monomer luminescence being observed regardless of the region of excitation (See Fig. 5(a))

Weak acidification produces no effect on the luminescence spectrum of the monomer. This observation is contrary to the situation observed in anilines\(^8\) or nitroaromatics\(^16\) where the luminescence spectra of the protonated and unprotonated species are quite different. It is also contrary to the effects on absorption spectra observed here. It seems reasonable to conclude, therefore, that protonated N,N-disalky-p-cyanoanilines dissociate in the excited luminescent states to yield the unprotonated excited monomer, a conclusion which also is borne out by the effects of protonation on excimer formation efficiencies\(^2\) in these same systems.
FIGURE 5
Total luminescence spectra at 77°K of NNDMPCA (a), excited in the dimer absorption band and (b) excited in the monomer absorption band.

______ 3-MP glass.
------- EPA glass.
-.-.-. Ethylalcohol glass.
....... Crystalline state.
The spectroscopic characteristics of the various emissions are tabulated in Table 3. It is seen that monomer and dimer emissions shift to lower energies as the solvent polarity increases; that the phosphorescence lifetime of the dimer, $\tau_p^D$, increases and that the associated quantum yield ratio, $(\varphi_p/\varphi_f)_D$, decreases with increasing polarity of both solvent and solute.

**DISCUSSION**

Intermolecular interactions exhibit great variety. In view of the fact that the molecules of interest here are highly dipolar in both their ground and excited states and that they exhibit some electronic transitions of very high extinction, we will restrict discussion to dipole-dipole interactions of static and transition moment type. We cannot, as other authors do, neglect static dipolar interactions; in fact, we go to the opposite extreme in our presumption of their dominance.

We adopt the following notations: $S_0^M, S_1^M, S_2^M, \ldots$, $T_1^M, T_2^M$ represents the manifold of monomer states; $[S_j^D, T_1^D]$ represents the manifold of dimer states; $[S_j^D, T_1^D]$ represent of the $S_0^M$ state; $\mu_e$ is the dipole moment of the $1L_a$ monomer (probably $S_2^M$) state; $\mu_T$ is the dipole moment of $T_1^M$, $M$ is the transition moment of the $1L_a \leftrightarrow 1A_1 (1S_2^M + 1S_0^M)$ transition; and $R$ is an intermolecular distance.

Since $T_1^M$ is of $3L_a$ type, we may assume that $T_1^D$ is of $3L_a$ parentage. As is clear from Table 3, the difference $\nu_p^M (0,0) - \nu_p^D (0,0)$ is greater than zero and increases with an increase of
<table>
<thead>
<tr>
<th>GLASS</th>
<th>$\lambda_{\text{exc}}$ (m\textmu)</th>
<th>$\tilde{\nu}_g(0,0)$ (cm$^{-1}$)</th>
<th>$\tilde{\nu}_p(0,0)$ (cm$^{-1}$)</th>
<th>$\tau_p$ (sec)</th>
<th>S-T Split (cm$^{-1}$)</th>
<th>$\varphi_p/\varphi_g$</th>
</tr>
</thead>
<tbody>
<tr>
<td>3-MP</td>
<td>290</td>
<td>31000</td>
<td>24650</td>
<td>2.13$\pm$0.13</td>
<td>5350</td>
<td>1.2</td>
</tr>
<tr>
<td>(8.76x10$^{-7}$)</td>
<td>330</td>
<td>27750</td>
<td>22800</td>
<td>0.62$\pm$0.01</td>
<td>4950</td>
<td>5.8</td>
</tr>
<tr>
<td>EPA</td>
<td>280</td>
<td>30750</td>
<td>24300</td>
<td>2.16$\pm$0.02</td>
<td>6450</td>
<td>1.02</td>
</tr>
<tr>
<td>(5.83x10$^{-4}$)</td>
<td>330</td>
<td>2700</td>
<td>22100</td>
<td>0.33$\pm$0.02</td>
<td>4900</td>
<td>1.36</td>
</tr>
<tr>
<td>ETOH</td>
<td>280</td>
<td>30500</td>
<td>24400</td>
<td>2.25$\pm$0.08</td>
<td>6100</td>
<td>1.043</td>
</tr>
<tr>
<td>(8.32x10$^{-5}$)</td>
<td>330</td>
<td>26600</td>
<td>21900</td>
<td>1.46$\pm$0.04</td>
<td>4700</td>
<td>0.06</td>
</tr>
<tr>
<td>Crystal</td>
<td>295</td>
<td>26100</td>
<td>21750</td>
<td>0.48</td>
<td>4350</td>
<td>0.493</td>
</tr>
</tbody>
</table>
solvent polarity. Since the transition moments of T-S transitions are quite negligible, it is immediately implied that
\[ \varphi_p^M(0,0) - \varphi_p^D(0,0) \approx \mu_2^2/R^3 - \mu_8^2/R^3 + B-A+.. \]
where B and A are solvent-solute interaction energies in T_D and S_D, respectively, and that \( \mu_T > \mu_g \).

The dimer fluorescence energy is more sensitive to solvent polarity than is that of the monomer fluorescence. Thus, we can conclude from Table 3 that \( \mu_e > \mu_g \). Since \( \mu(1_{L_B}) \) is not expected to differ much from \( \mu(1_{A_1}) \), we might infer, therefore, that \( \mu_e \) pertains to a \( 1_{L_a} \) state. If so, we may write
\[ \varphi^{1_{L_a} + 1_{S_0}} - \varphi_f \approx \mu_e^2/R^3 + \mu_2^2/R^3 - \mu_8^2/R^3 + C-A+.. \]
If, further, because of the presumed \( L_a \) nature of both excited state dimer species, we assume that \( \mu_T = \mu_e \), we find \( B = C \) and can write
\[ \{\varphi_p^M(0,0) - \varphi_p^D(0,0)\} - \{\varphi^{1_{L_a} + 1_{S_0}} - \varphi_f^D\} \approx M^2/R^3 \approx 4000 \text{cm}^{-1} \]
The computed value of \( M^2/R^3 \) for the \( 1_{L_a} \) state is (see Table 4) 5072 cm\(^{-1}\) at \( R=4.8\AA \) & 3562 cm\(^{-1}\) at \( R=4.5\AA \), in fair agreement with the experimental value of \( \sim 4000 \text{cm}^{-1} \).

The enhancement of \( \varphi_p/\varphi_f \) which occurs upon dimerization, the low extinction of the \( \sim 29000 \text{cm}^{-1} \) dimer absorption band, and the considerations of the previous paragraph, all indicate that molecular exciton coupling is effective and that the \( 1_{S_D} \) \( \sim 1_{S_0} \) transition is forbidden\(^{18-20}\). This conclusion is compatible with a dimeric sandwich structure for \( S_D \) in which the transition dipoles of
TABLE IV

DIPOLE-DIPOLE INTERACTION ENERGIES IN NNDMPCA DIMER

<table>
<thead>
<tr>
<th>Interaction Term (a)</th>
<th>Energy (cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>R=4Å</td>
</tr>
<tr>
<td>( \mu_g^2/R^3 )</td>
<td>3430</td>
</tr>
<tr>
<td>( \mu_T^2/R^3 )</td>
<td>5280</td>
</tr>
<tr>
<td>( \mu_e^2/R^3 )</td>
<td>12306</td>
</tr>
<tr>
<td>( M^2/R^3 )</td>
<td>5072</td>
</tr>
</tbody>
</table>

a) \( \mu_g \) is taken as 6.6D; \( \mu_T \) was calculated from \( \nu_p^{M-D} = \nu_p^{M} - \nu_p^D = 1850 \text{ cm}^{-1} \) \( \Rightarrow \mu_T^2/R^3 - \mu_g^2/R^3 \), where 1850 cm⁻¹ is the triplet separation in 3-MP glass; all calculations assumed that \( \mu_e = 12.5 \text{D} \), as is given in Ref. 2 (However, this value may be too large; at any rate, it is correct that \( \mu_e \geq \mu_T \)); a value \( M \approx 8 \text{D} \) was deduced from the f-number and frequency of the 33000 cm⁻¹ absorption band of NNDMPCA.
the individual $\frac{1}{2} S_2^M$ components are out-of-phase. The resultant energy diagram, replete with all the prejudices of this section, is shown in Fig. 6.

A list of various interaction energies is given in Table 4. The energy terms are sensitively dependent on \( R \) but, for any specific \( R \), lie in the order \( \frac{\mu_1^2}{R^3} > \frac{\mu_2^2}{R^3} > \frac{\mu_3^2}{R^3} > \frac{\mu_6^2}{R^3} \). The value of \( V(\frac{1}{2} L_a - \frac{1}{2} S_0^M) = \frac{V_f^D}{2} \) for NNDMPCA in a 3-methylnpentane glass (where C & A may be taken to be quite small and to cancel each other) is 5600cm\(^{-1}\). The computed value (see Table 4) is 19228, 14054 \\& 10746cm\(^{-1}\) at \( R = 4, 4.5 \& 5 \AA \), respectively, of an exactly-mated sandwich structure. The discrepancy of the observed and computed data is readily corrected by introducing an angular rotation or sideways displacement of one molecule with respect to the other in the sandwich.

In sum, while we have shown that dipole-dipole interactions can account for the observed set of dimer energy levels and that molecular exciton considerations can rationalize the observed absorption and emission probabilities of various dimer transitions, we have by no means proved such. Finally, the observed intensification of the $1S_0^D \leftarrow 1S_0^D$ transition in polar solvents (joined as it is with lower values of the association constant, \( K \)) forces us to conclude that dimer-solvent interactions are also important in determining the spectroscopic behavior of the dimer.
FIGURE 6

Energy level diagram for NNDMPCA monomer and dimer. The solid horizontal bars are experimental state energies. Dashed horizontal bars are estimated energies of unobserved states. Vertical lines connecting the solid horizontal bars represent observed electronic transitions.
REFERENCES


19. E.G. McRae and M. Kasha, "Physical Processes in Radiation Biology", [L. Augenstei...
VITA

Omar Soliman Khalil was born in Koom Hamada, Egypt on April 23, 1944. He received his secondary education at Damanhour Secondary School, Damanhour, Egypt from which he graduated in 1960.

He, then, began his college training and, subsequently, received a B.Sc. degree in chemistry from the Faculty of Science, Alexandria University, Alexandria, Egypt in 1964. After his graduation he taught undergraduate chemistry and pursued his graduate work. After getting his M.Sc. degree in 1968, he was awarded a study leave to the United States.

In September 1968, he joined the Graduate School of the Louisiana State University where he is presently a candidate for the degree of Doctor of Philosophy.

He is married to Hoda Abu El-Enein and they have a smart little boy, Ashraf, of whom they are very proud.
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Major Field: Chemical-Physics

Title of Thesis: Electronic Spectroscopy of Highly-Polar Aromatics

Approved:

\[\text{Signature} \]
Major Professor and Chairman

[Signature]
Dean of the Graduate School

EXAMINING COMMITTEE:

[Signature]

[Signature]

[Signature]

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Date of Examination:

November 30, 1972