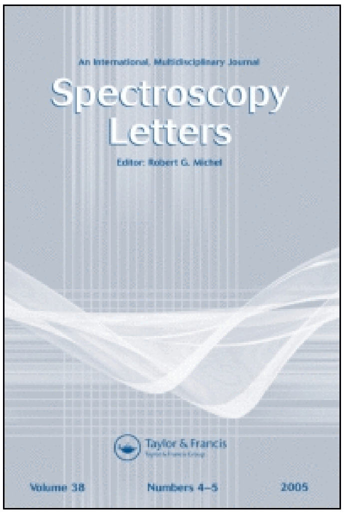

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Electronic Spectroscopy of Highly-Polar Aromatics. VI. A Self-Complex of N,N-Dialkyl-p-Cyanoanilines

Omar S. Khalil[a][b]; R. H. Hofeldt[a][c]; S. P. McGlynn[a]
[a] Department of Chemistry, The Louisiana State University, Baton Rouge, Louisiana [b] Department of Chemistry, Rutgers University, New Brunswick, New Jersey [c] Department of Chemistry, Boston University, Boston, Massachusetts

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ELECTRONIC SPECTROSCOPY OF HIGHLY-POLAR AROMATICS

VI. A SELF-COMPLEX OF N,N-DIALKYL-p-CYANOANILINES*

by

Omar S. Khalil**, R. H. Hofeldt≠ and S. P. McGlynn

Department of Chemistry
The Louisiana State University
Baton Rouge, Louisiana 70803

ABSTRACT

The absorption and luminescence spectra of N,N-dialkyl-p-cyanoanilines are reported. A weak absorption band at ~ 29000cm^{-1} is assigned to a self-complex of these molecules. Assuming a dimeric form for the self-complex, the association constant is $50 \leq K \leq 150$ 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 $T_1^D \rightarrow {}^1S_0^D$ and ${}^1S_1^D \rightarrow {}^1S_0^D$ 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.

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**Present address: Department of Chemistry
Rutgers University
New Brunswick, New Jersey 08903

≠Present address: Department of Chemistry
Boston University
147 Bay State Road
Boston, Massachusetts 02215

INTRODUCTION

The total luminescence spectrum of solutions of N,N-dialkyl-p-cyanoanilines may consist[1] of five different emissive events: Two phosphorescences and three fluorescences. The longest wavelength fluorescence has been described in some detail[2] and has been assigned to an excimer luminescence. The fluorescence and phosphorescence of shortest wavelengths refer to monomer emission events of probable $^1L_b \rightarrow {}^1S_0$ 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[1-4] 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 $33000 \leq \bar{\nu} \leq 34500 \text{cm}^{-1}$ with $\epsilon \simeq 2 \times 10^4 \ell\, m^{-1} \text{cm}^{-1}$; and a weak band of much lower absorptivity in the region $29000 \leq \bar{\nu} \leq 31000 \text{ cm}^{-1}$.

The intensity of this weak band is $\sim 10^2$ times less than that of the 33000cm^{-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°K.

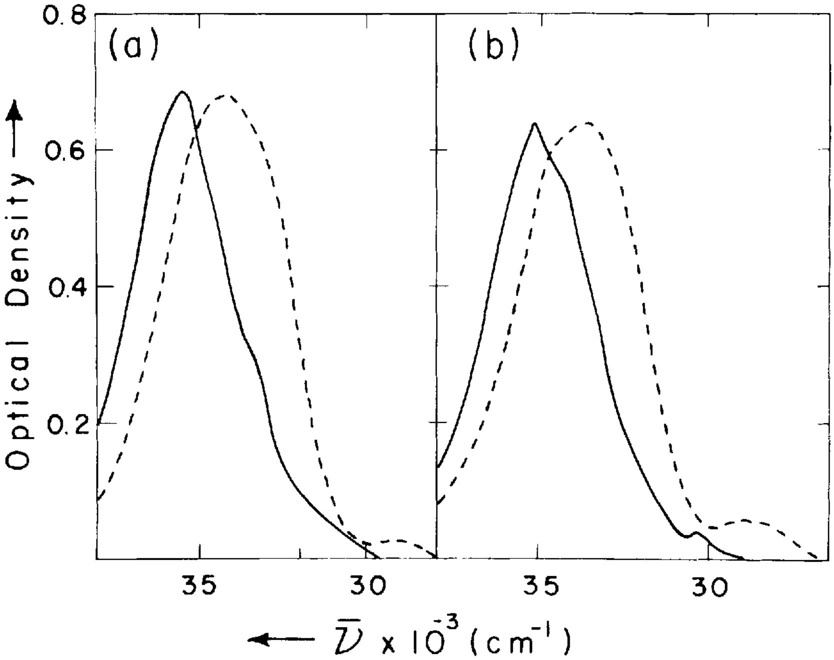

Fig. 1. Absorption spectra of (a), NNDMPCA and (b), NNDEPCA at 25^{0}C.

______ In methylcyclohexane

------- In ethylalcohol

It is this weak band which we assign to the $^1S_1 \leftarrow {}^1S_0$ 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 $^1L_b \leftarrow {}^1S_0$ and $^1L_a \leftarrow {}^1S_0$ excitations. Since the ^1L_a state possesses a significant charge transfer characteristic and is highly polar, it is also thought[5-7] that these two states, ^1L_a & ^1L_b, can interchange their relative energy positions and that, in highly-polar solvents, the $^1L_a \leftrightarrow {}^1S_0$ can be of lower energy than the $^1L_b \leftrightarrow {}^1S_0$

transition. Indeed, that emission now identified[2] as an excimer fluorescence was previously assigned[5-7] to a $^1L_a \rightarrow {}^1S_0$ process of a highly-solvated NNDMPCA monomer.

In slightly acid media, the ~ 29000cm^{-1} band dissappears and the intensity of the ~ 33000cm^{-1} band decreases. These effects are exactly reversible upon neutralization with NH_4OH 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 ~ 33000cm^{-1} band is readily rationalized[8]: Protonation of the amino group leads to a decrease of the charge transfer characteristic of the $^1L_a \leftarrow {}^1S_0$ monomeric event and removes this transition to a new energy location. The disappearance of the ~ 29000cm^{-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 ~ 33000 nor the ~ 29000cm^{-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 ~ 29000cm^{-1} band refers to some sort of solute-solute association (or self-complex) and that only the ~ 33000cm^{-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 antiparallel; and it is only to be expected that the similar (and considerably more-polar) N,N-dialkyl-p-cyanoanilines would do likewise.

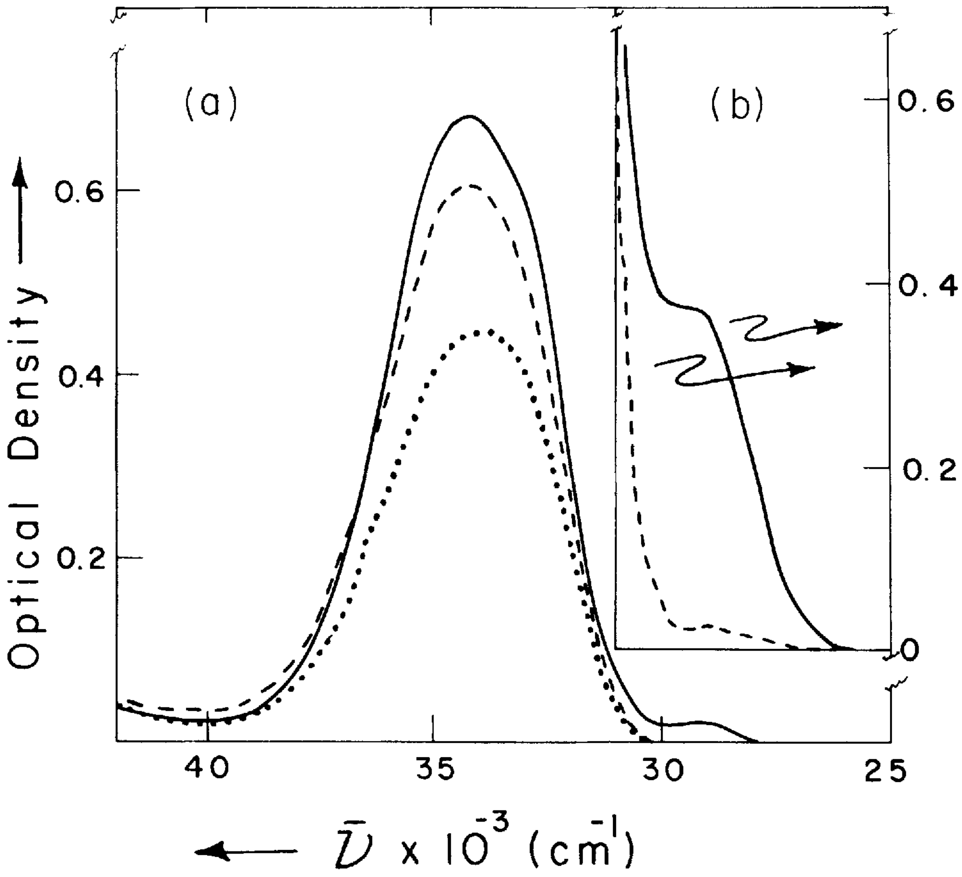

Fig. 2. Room temperature absorption spectra of NNDMPCA in neutral and acid media.

______ Ethylalcohol

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

.... Ethylalcohol, 5% hydrochloric acid.

sets (a) and (b) refer to 0.1 and 1cm cells, respectively.

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

$$D = \epsilon c \ell (1-\alpha)$$

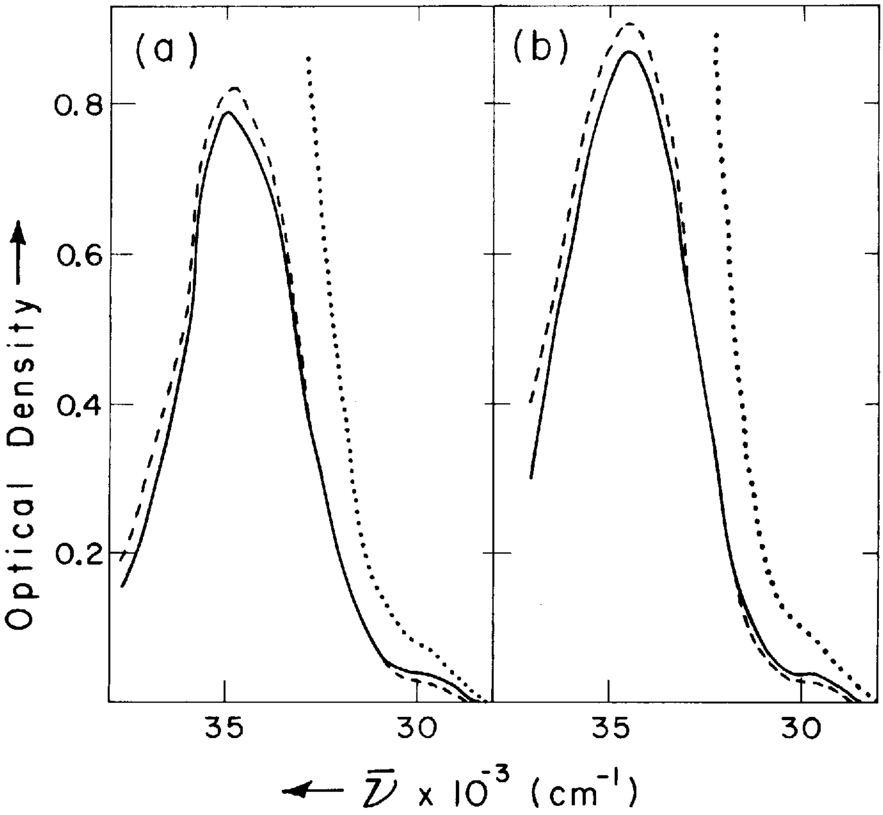

Fig. 3. Effect of concentration on room temperature absorption spectra of NNDMPCA in different solvents.

(a) .... 5.97×10^{-4}M, 0.1cm cell.

______ 2.97×10^{-4}M, 0.1cm cell.

------- 1.19×10^{-5}M, 2.5cm cell.

In an ethylacetate solvent.

(b) .... 8.36×10^{-4}M, 0.1cm cell.

______ 3.34×10^{-4}M, 0.1cm cell.

------- 1.34×10^{-5}M, 2.5cm cell.

In a p-dioxane solvent.

where ϵ & c are monomer extinction and concentration, respectively; where ℓ is path length; and α is the degree of association. A monomer-dimer equilibrium leads to

$$D = \epsilon c \ell - D^2 K / \epsilon \ell$$

Hence, if the absorption spectra of two solutions of different c but constant $c\ell$ are obtained, it follows that

$$\Delta D = D_1 - D_2 = (D_2^2/\ell_2 - D_1^2/\ell_1)K/\epsilon$$

Since ϵ 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 $K \simeq 10^2 \ell/m$. 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^oK 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 $\sim 1750 cm^{-1}$. Since the C≡N stretching frequency of the $^1S_0$ state lies[14,15] at $2230 cm^{-1}$ in NNDMPCA, since the symmetric ring-breathing vibration lies[15] at $\sim 1600 cm^{-1}$, 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 $\sim 1750 cm^{-1}$ frequency represents a C≡N stretching mode in the excited state(s).

-----The intensity of the longer-wavelength progression II increases considerably relative to progression I as the concentration of the

TABLE 1

EQUILIBRIUM CONSTNAT FOR THE DIMER OF NNDMPCA AT 25^{o}C

Solvent	c	ℓ^{a}	$\epsilon\ell^{b}$	D	ΔD	K/ϵ	ϵ	K^{c}
	(m/ℓ)	(cm)	(x10^{-5})			(x10^{-3})	(x10^{-4})	(x10^{-2})
Dioxane	3.34x10^{-4}	0.1		0.86			2.59	
			3.34		0.035	4.9		1.3
	1.34x10^{-5}	2.5		0.90			2.69^{d}	
Ethylacetate	2.99x10^{-4}	0.1		0.79			2.64	
			2.99		0.03	5		1.4
	1.2 x10^{-5}	2.5		0.82			2.74^{d}	
Acetonitrile	2.84x10^{-4}	0.1		0.73			2.58	
			2.84		0.012	2.3		0.6
	1.14x10^{-5}	2.5		0.74			2.61^{d}	
Dimethyl-formamide	2.96x10^{-4}	0.1		0.73			2.48	
			2.96		0.015	3		0.8
	1.18x10^{-5}	2.5		0.75			2.54^{d}	

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 ~ 29000cm^{-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 $^1L_b \leftarrow {}^1S_0$ 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 ^1L_a & ^1L_b states of these latter molecules are heavily mixed by vibronic interactions. This, in view of the energetic proximity of the ^1L_a & ^1L_b states, is certainly possible and is the only way we can rationalize the occurrence of a dominant C≡N stretching frequency in a $^1L_b \leftarrow {}^1S_0$ transition.

---

a) Optical path in cm.

b) Molar extinction coefficient in ℓ m^{-1} cm^{-1}.

c) Equilibrium constant in ℓ m^{-1}.

d) Molar extinction coefficient for the solution of lower concentration, in which it is assumed that dimer concentration is minimal.

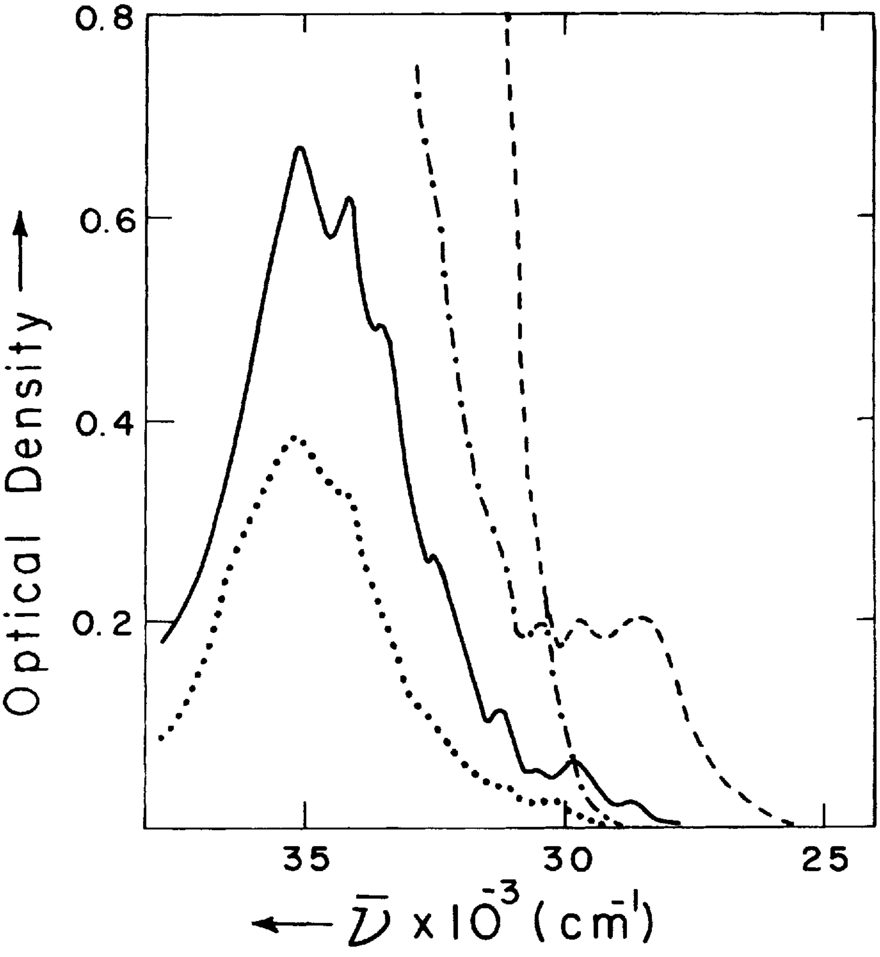

Fig. 4. Absorption spectra of NNDEPCA in 3-methylpentane.

.... 2.3×10^{-5}M, 0.5cm cell at 25°C.

______ Same solution, 0.4cm cell at 77°K.

-.-.-.- 1.15×10^{-4}M, 0.5cm cell at 25°C.

------- Same solution, 0.4cm cell at 77°K.

LUMINESCENCE SPECTRA

The low-temperature luminescence spectra of glassy solutions are shown in Fig. 5. Excitation in the monomer absorption region yields the fluorescence and phosphorescence of Fig. 5(b). The

TABLE 2

VIBRATIONAL ANALYSIS OF THE ABSORPTION SPECTRA OF FIGURE 4

Progression I			Progression II		
$\bar{\nu}$ (cm^{-1})	$\Delta\bar{\nu}$ (cm^{-1})	$\Delta\bar{\nu}/n$ (cm^{-1})	$\bar{\nu}$ (cm^{-1})	$\Delta\bar{\nu}$ (cm^{-1})	$\Delta\bar{\nu}/n$ (cm^{-1})
29630	0,0		28777	0,0	0.00
31056	1426	1426	30534	1757	1757
33333	3703	1851	32258	3481	1740
34843	5211	1737	34014	5237	1745
	Average = 1723			Average = 1745	

phosphorescence is of relatively long lifetime, $\tau_p \simeq 2$ 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, $\tau_p \simeq 0.5$ sec , and the fluorescence is essentially identical to that observed under similar excitation conditions in fluid solutions at 25°C which exhibit absorptivity at $\sim 29000 cm^{-1}$.

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

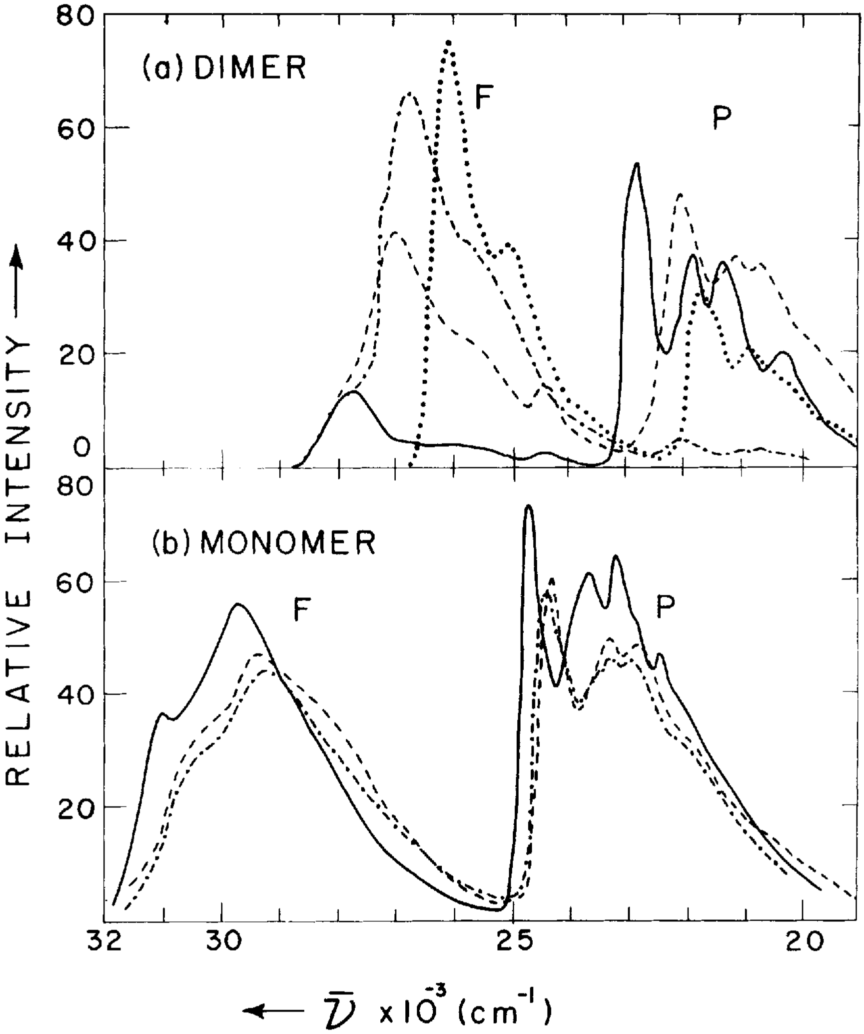

Fig. 5. Total luminescence spectra at 77°K of NNDMPCA (a), excited in the dimer absorption band and (b) excited in the monomer absorption band.

______ 3-MP glass.

------- EPA glass.

-.-.-.- Ethylalcohol glass.

.... Crystalline state.

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-dialky-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.

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, τ_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[17-20], 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, ..., T_1^M, T_2^M represents the manifold of monomer states; $\{S_j^D, T_i^D\}$ represents the manifold of dimer states; μ_g is the dipole moment of the S_0^M state; μ_e is the dipole mement of the ^1L_a monomer (probably S_2^M) state; μ_T is the dipole moment of T_1^M, M is the transition

TABLE 3

LUMINESCENCE CHARACTERISTICS OF THE NNDMPCA MONOMER AND DMER

GLASS (conc.,m/1)	λ_{exc} (mμ)	$\bar{\nu}_f(0,0)$ (cm^{-1})	$\bar{\nu}_p(0,0)$ (cm^{-1})	τ_p (sec)	S-T Split (cm^{-1})	φ_p/φ_f
3-MP	290	31000	24650	2.13±0.13	5350	1.2
($8.76x10^{-7}$)	330	27750	22800	0.62±0.01	4950	5.8
EPA	280	30750	24300	2.16±0.02	6450	1.02
($5.83x10^{-4}$)	330	2700	22100	0.33±0.02	4900	1.36
ETOH	280	30500	24400	2.25±0.08	6100	1.043
($8.32x10^{-5}$)	330	26600	21900	1.46±0.04	4700	0.06
Crystal	295	26100	21750	0.48	4350	0.493

moment of the ${}^1L_a \leftarrow {}^1A_1$ (${}^1S_2^M \leftarrow {}^1S_0^M$) transition; and R is an intermolecular distance.

Since T_1^M is of ${}^3L_a$ type [5,15], we may assume that T_1^D is of ${}^3L_a$ parentage. As is clear from Table 3, the difference $\bar{\nu}_p{}^M(0,0) - \bar{\nu}_p{}^D(0,0)$ is greater than zero and increases with an increase of solvent polarity. Since the transition moments of $T \leftarrow S$ transitions are quite negligible, it is immediately implied that

$$\bar{\nu}_p{}^M(0,0) - \bar{\nu}_p{}^D(0,0) \simeq \mu_T^2/R^3 - \mu_g^2/R^3 + B - A + ..$$

where B and A are solvent-solute interaction energies in $T_1{}^D$ and $S_0{}^D$, 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 $\mu({}^1L_b)$ is not expected to differ much from $\mu({}^1A_1)$, we might infer, therefore, that μ_e pertains to a ${}^1L_a$ state. If so, we may write

$$\bar{\nu}({}^1L_a \leftarrow {}^1S_0) - \bar{\nu}_f^D \simeq \mu_e^2/R^3 + M^2/R^3 - \mu_g^2/R^3 + C - A + ..$$

If, further, because of the presumed L_a nature of both excited state dimer species, we assume that $\mu_T \simeq \mu_e$ we find $B \simeq C$ and can write

$$\{\bar{\nu}_p{}^M(0,0) - \bar{\nu}_p{}^D(0,0)\} - \{\bar{\nu}({}^1L_a^M \leftarrow {}^1S_0^M) - \bar{\nu}_f^D\} \simeq M^2/R^3 \simeq 4000\text{cm}^{-1}$$

The computed value of M^2/R^3 for the ${}^1L_a$ state is (see Table 4) 5072cm^{-1} at $R \doteq 4A^o$ & 3562cm^{-1} at $R=4.5A^o$, in fair agreement with the experimental value of ~ 4000cm^{-1}.

The enhancement of φ_p/φ_f which occurs upon dimerization, the low extinction of the ~ 29000cm^{-1} dimer absorption band, and the considerations of the previous paragraph, all indicate that molecular exciton coupling is effective and that the ${}^1S_1^D \leftrightarrow {}^1S_0^D$ transition is forbidden[18-20]. This conclusion is compatible with a

TABLE IV

DIPOLE-DIPOLE INTERACTION ENERGIES IN NNDMPCA DIMER[a]

Interaction Term (a)	Energy (cm^{-1}) R=4A°	R=4.5A°	R=5A°
μ_g^2/R^3	3430	2409	1756
μ_T^2/R^3	5280	4259	3606
μ_e^2/R^3	12306	8642	6300
M^2/R^3	5072	3562	2596

a) μ_g is taken as 6.6D; μ_T was calculated from $\bar{\nu}_p^M - \bar{\nu}_p^D = 1850 cm^{-1} \simeq \mu_T^2/R^3 - \mu_g^2/R^3$, where $1850cm^{-1}$ is the triplet separation in 3-MP glass; all calculations assumed that μ_e = 12.5D, 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 $M \simeq 8D$ was deduced from the f-number and frequency of the $33000cm^{-1}$ absorption band of NNDMPCA.

dimeric sandwich structure for S_1^D in which the transition dipoles of the individual ${}^1S_2^M$ 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 $\mu_e^2/R^3 \geq \mu_T^2/R^3 > M^2/R^3 > \mu_g^2/R^3$. The value of $\bar{\nu}({}^1L_a^M \leftarrow {}^1S_0^M) - \bar{\nu}_f^D$ for NNDMPCA in a 3-methylpentane glass (where C & A may be taken to be quite small and to cancel each

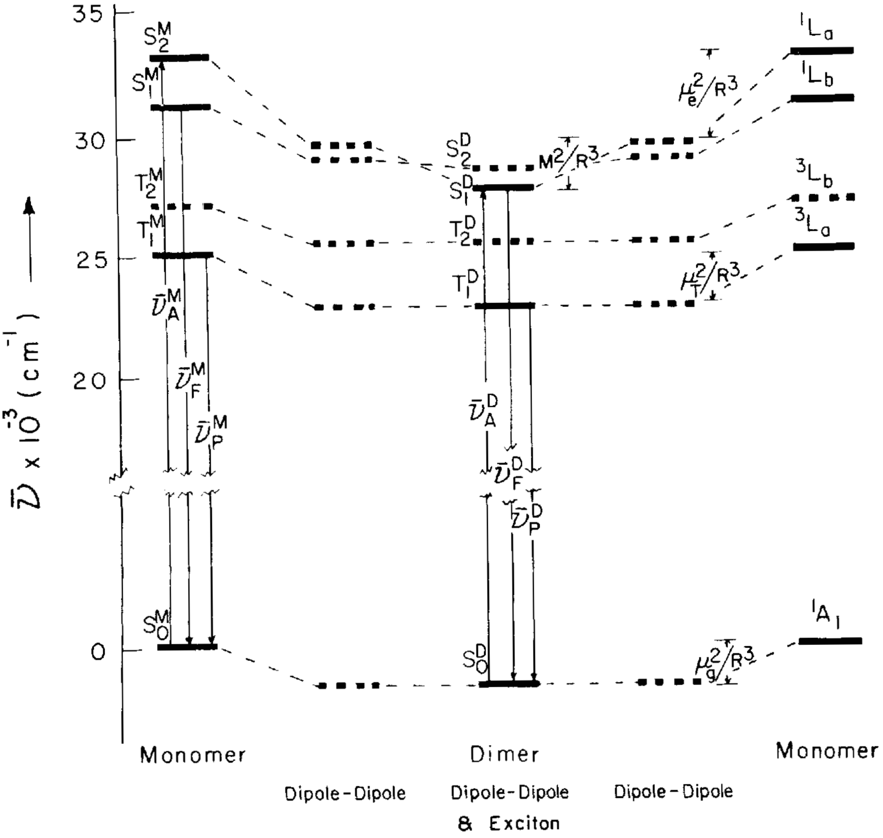

Fig. 6. Energy level diagram for NNDMPCA monomer and dimer. The solid horizontal bars are experimental state energies. Dashed horizontal bars are estimated energies of unobserved states. Vertical lines connecting the solid horizontal bars represent observed electronic transitions.

other) is 5600cm^{-1}. The computed value (see Table 4) is 19228, 14054 & 10746cm^{-1} at R = 4,4.5 & 5Å, 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 ${}^1S_1^D \leftarrow {}^1S_0^D$ 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.

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