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Triplet Photophysics of Multichromophoric Molecules. A Study of Poly(*N*-vinylcarbazole) and *meso*-2,4-Dicarbazolylpentane in Fluid Solutions

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ABSTRACT: Delayed luminescence and transient absorption experiments have been carried out on fluid solutions of poly(*N*-vinylcarbazole) (PVCz) and *meso*-2,4-dicarbazolylpentane (DCP) in benzene, cyclohexane, and 1,1-dimethylformamide (DMF). The delayed emission spectra of dilute solutions of DCP in all the solvents are similar and consist of excimeric delayed fluorescence (EDF) with a small contribution from monomeric delayed fluorescence. For PVCz in both benzene and DMF the delayed emission consists primarily of EDF at a delay of 1 μs, but this signal decays away quickly leaving the excimeric phosphorescence band at longer delay times. The transient absorption spectra for DCP depend markedly upon the solvent. In benzene and cyclohexane the absorption is due to the carbazolyl triplet state, but in DMF absorbance bands due to the triplet and to radical cations and anions are found. Transient absorption spectra were also recorded for PVCz in benzene and DMF. Again, ionic species predominate in DMF and triplet states predominate in benzene, while the triplet excimer is present in both solutions. It is concluded that a conformation suitable for triplet excimer formation can be achieved within PVCz polymeric coils but cannot be formed intramolecularly within DCP.

Introduction

Recent work from these laboratories[1] has shown that UV laser (XeCl) photoexcitation of *N*-ethylcarbazole (NEC) in fluid solutions at ambient temperature produces transient species having interesting properties. Relying upon spectral assignments made by Yamamoto and co-workers,[2] radical cations of carbazole were detected as transient species following 308 nm laser pulses in the microsecond time range when high dielectric solvents were used. The carbazolyl cation was observed even in the absence of added electron acceptors. In addition, transient absorption bands ascribed to the radical anion of the carbazolyl species were found based upon earlier studies[3,4] of photoexcited carbazole solutions. Furthermore, it appears that triplet states and excited singlet states can be formed by recombination of these ionic species.[5] In addition, both excimeric delayed fluorescence (EDF) and excimeric phosphorescence were found in high dielectric solvents such as ethanol, but only monomeric emissions were found in low dielectric solvents such as cyclohexane. Again these assignments were made in accord with earlier observations of these excimeric species.[6,7] If we use $^2Cz^+$ and $^2Cz^-$ to symbolize the carbazolyl radical cation and anion, respectively, the formation of these species by laser photoexcitation may be represented by a multiphoton process,

$$^1Cz_0 + X \xrightarrow{nh\nu} \{^2Cz^+ ... ^2X^-\} \quad (1)$$

where $^1Cz_0$ is a ground-state NEC molecule, $^2X^-$ may be either $^2Cz^-$ or a solvent anion, with the bracketed species representing a geminate ion pair. In a high-viscosity, high-dielectric solvent such as glycerol no delayed excimer fluorescence was observed, and so it was concluded that material diffusion is a critical step in excimer formation. There is precedent[8] for invoking the intermediate formation of a cation dimer, $^2D^+$, followed by ion recombination to form the singlet excimer by

$$^2Cz^+ + {^1Cz_0} \rightarrow {^2D^+} \quad (2)$$

$$^2D^+ + {^2X^-} \rightarrow {^1D^*} + X \quad (3)$$

where $^1D^*$ is the singlet excimer.

It has been noted previously that back electron transfer from anion to cation may occur over several molecular diameters[7] so that a process such as

$$^2Cz^+ + {^2Cz^-} \rightarrow {^1Cz^*} + {^1Cz_0} \quad (4)$$

would not necessarily lead to excimer formation since the reaction of $^1Cz^*$ with the neighboring ground-state carbazole would have to occur within a few nanoseconds in order to compete with first-order relaxation of the excited singlet state to the ground state. There are at least two situations, however, for which this conclusion may not be valid. One example is a bichromophoric molecule in which the two Cz groups are at fixed positions which are suitable for excimer formation. If these two Cz groups happened to be oppositely charged, fast intramolecular ion recombination could very well lead to singlet excimer formation. Another exception could be realized if the back electron transfer produced a triplet state instead of an excited singlet directly

$$^2Cz^+ + {^2Cz^-} \rightarrow {^3Cz^*} + {^1Cz_0} \quad (5)$$

or indirectly

$$^2Cz^+ + {^2Cz^-} \rightarrow {^1Cz^*} + {^1Cz_0} \rightarrow {^3Cz^*} + {^1Cz_0} \quad (6)$$

In this case some tens of microseconds are available for the conversion

$$^3Cz^* + {^1Cz_0} \rightarrow {^3D^*} \quad (7)$$

to occur before the triplet state is lost by relaxation or quenching. In fact, it has been found in earlier work[1] that excimeric phosphorescence is produced upon UV laser excitation of NEC even in high-viscosity glycerol solutions, thus indicating the viability of this mechanism. If eqs 5 and 6 represent a credible pathway for the formation of $^3D^*$, it is only because the ion recombination provides a way to place a ground-state molecule

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near the newly formed triplet. This notion has prompted us to consider the potential for triplet excimer formation in multichromophoric molecules. It is well-known, of course, that solid films of poly(*N*-vinylcarbazole) emit an excimeric phosphorescence at 77 K.[9] Whether or not a similar emission occurs in fluid solutions at ambient temperature is not known, but since the vinyl polymer represents a system of high local chromophore density, it would not be surprising to find a rather prominent excimer phosphorescence.

In order to provide answers to these questions, a detailed spectroscopic and kinetic investigation of triplet states in multichromophoric compounds containing the carbazolyl species has been carried out. Besides poly(*N*-vinylcarbazole) (PVCz) the particular molecule chosen for study was *meso*-2,4-dicarbazolylpentane (DCP). DCP was selected since previous work[4] has demonstrated its propensity to form singlet excimers upon photoexcitation in fluid solutions at ambient temperature. Since the influence of intermediate ion formation is also of interest,[10,11] the photophysical work has been carried out in benzene and cyclohexane, representing typical low dielectric solvents, and *N,N*-dimethylformamide (DMF), a typical high dielectric solvent.

Experimental Section

Purification of Chemicals. Samples of DCP were obtained from Prof. F. DeSchryver of Catholic University, Leuven, Belgium, and from Prof. M. Yamamoto of Kyoto University, Kyoto, Japan. They were used without further purification. Samples of PVCz were prepared in connection with earlier work in these laboratories.[12] They had been purified by multiple reprecipitations using benzene as a solvent and methanol as a nonsolvent and were not subjected to additional treatment in connection with the present study. Benzene and cyclohexane were refluxed and distilled twice from concentrated H_2SO_4. The distillate was washed three times with 5% NaOH and three times with water. It was then refluxed and distilled from P_2O_5, distilled from CaH_2, and finally stored over Linde 4A molecular sieves. The middle 75% was retained from all distillations. Acetonitrile (AcN) was shaken with Linde 4A molecular sieves and then with CaH_2 until no hydrogen gas evolved. It was then refluxed and fractionally vacuum distilled twice from CaH_2, collecting the center fraction. The final distillate was stored over Linde 4A molecular sieves. *N,N*-Dimethylformamide (DMF) was shaken with $MgSO_4$ and then vacuum distilled, collecting the center fraction. It was then stored over Linde 4A molecular sieves. Finally, 2-methyltetrahydrofuran (MTHF) was treated with $LiAlH_4$ and fractionally distilled.

Sample Preparation. All samples were prepared in 5 or 10 mL volumetric flasks at the desired concentrations and then transferred to 1 cm rectangular optical cells with quartz walls. The solutions were capped with a rubber septum to reduce solvent evaporation, and then argon was purged through the solution for at least 20 min by using syringe needles as entrance and exit ports. Samples were also prepared by degassing under vacuum using multiple freeze–pump–thaw cycles. Final pressures of 10^{-6} Torr were achieved, and the samples were sealed off under vacuum using a hand torch.

Transient Absorption Spectra, Emission Spectra, and Decay Kinetics. Details of these experiments have been reported in recent publications from these laboratories[5] and so will be described here only briefly. Transient absorption spectra and emission spectra were recorded using a Princeton Instruments optical multichannel analyzer interfaced with a laboratory computer. The detector was a Princeton Instruments Model IRY-700-S/B diode array. This was placed at the exit focal plane of a Spex Model 1681C spectrograph. The detection was gated with either a Princeton Instruments FG-100 or PG-10 pulse generator. The former has a variable gate width between 5 ns and 2.5 μs, and the latter produces gate widths from 180 ns to 6 ms. The excitation source in all of these experiments was a Questek Model 2110 XeCl excimer laser. Typical laser pulse energies of 7 mJ at 308 nm and with a 10 ns width at half-height were used. For transient absorption spectra the probe beam from a xenon lamp was chopped using a rotating disk and entered the sample at right angles to the excitation beam. Only the 0.5 mm layer of solution adjacent to the cell wall facing the laser pulse was probed in these experiments. This was done in order to assure spatial uniformity of the concentration of the transient being examined. An LED detector system was used on the chopper to initiate the timing sequence for firing the laser and triggering the detector. The kinetics of transient decay were recorded at a fixed wavelength of the probing light using a Spex 1680B monochromator and a Hamamatsu R928 photomultiplier tube. The Xe lamp was also used as the probe beam for these experiments, and a LeCroy Model 9410 digital oscilloscope, providing time resolution to 10 ns, was used to record the decay signals and transmit the data onto the computer. A few experiments were carried out at low temperature using an APD Cryogenic Model CS-202 Displex closed-cycle helium system.

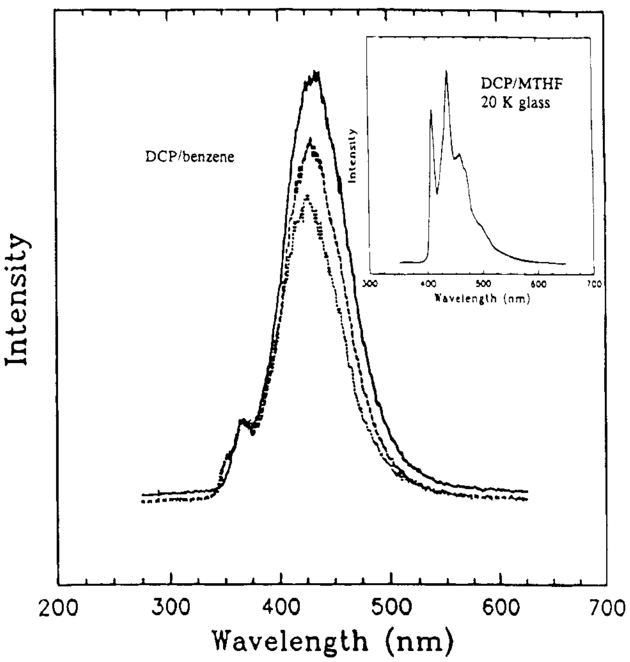

Figure 1. Delayed emission spectrum of DCP in benzene at 1×10^{-3} M (upper), 3×10^{-4} M (middle), and 5×10^{-5} M (lower) using a 1 μs delay and a 6 ms gate. The inset is a phosphorescence spectrum of DCP (10^{-3} M) in MTHF glass at 20 K using a 6 ms gate and a 7 ms delay.

Experimental Results

A. Emission Spectra. The emission spectra for solutions of DCP in benzene covering a 20-fold range of concentrations are presented in Figure 1. A broad structureless band centered at 430 nm is the prominent feature of these spectra. Smaller subsidiary bands near 365 nm are also present. These weaker bands are probably components of the monomeric delayed fluorescence, whereas the 430 nm band corresponds to the EDF. Similar spectra are obtained using cyclohexane as the solvent, but the main band is centered at 420 nm. The inset is a phosphorescence spectrum of DCP in MTHF glass at 20 K. It is useful to note that this low-temperature phosphorescence spectrum is essentially identical to that of the monochromophoric species, NEC, recorded under similar conditions. Using the 10^{-3} M solution of DCP, time-resolved spectra were also recorded up to 133 μs after the excitation pulse, and no spectral changes were apparent with increasing delay time.

It may be recalled that DCP exists in two isomeric forms *meso* and *racemic d,l* and in this investigation

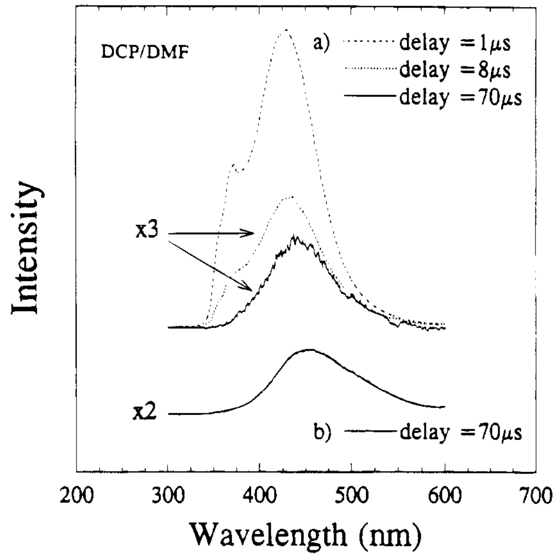

Figure 2. Delayed emission spectra of DCP in DMF at various delay times using a 10 μs gate: (a) 10^{-4}M; (b) 5×10^{-3} M.

only the former was studied. Previous reports[4,13] on the prompt fluorescence of these compounds have shown two types of excimeric fluorescence. One, thought to be due to a sandwich alignment of chromophores, has an emission centered at 420 nm. The other, apparently due to a staggered alignment of chromophores, has a fluorescence maximum near 375 nm. The *meso* isomer of DCP[4] forms the sandwich excimer, while the *racemic d,l* isomer[13] forms the staggered species having a partial overlap of the aromatic rings. This latter excimer is often described as the "second excimer". Thus, the 430 and 420 nm delayed emissions from DCP in benzene and cyclohexane, respectively, have been assigned to the sandwich excimer conformation. It should be noted that no monomeric or excimeric phosphorescence was found in benzene or cyclohexane solutions of DCP and that concentrations were kept at low levels to reduce the number of intermolecular interactions.

Figure 2 is a collection of time-resolved delayed emission spectra of DCP using DMF as the solvent. Here, the spectrum at all delay times shown is very similar to that recorded in benzene, except when concentrations are as high as 5×10^{-3} M. In these higher concentration samples the main band shifts to longer wavelengths (450 nm) when delay times are greater than 70 μs. It should be noted that some of the degassed DMF solutions exhibited a slight color change after prolonged exposure to laser pulses, indicating that a low-efficiency photochemical process may be occurring. At this time attempts to isolate and identify any products from these solutions have been unsuccessful apparently due to the extremely small quantities formed. A spectrum was also recorded of a degassed solution of DCP in acetonitrile. After exposure to the laser excitation this solution also became yellow in color and emitted a strong luminescence with a peak near 480 nm. At this time we are not sure if the emission is from a photoproduct or from a carbazolyl excited state.

In Figure 3 time-resolved delayed luminescence spectra of degassed PVCz solutions in benzene and in DMF are presented. For the polymer both the sandwich singlet excimer and the second excimer are possible emitting species, leading to a complicated spectrum. In both solvents the most prominent peak near 420 nm is undoubtedly due to delayed fluorescence from the sandwich species and the shoulder near 375 nm to delayed fluorescence from the second excimer. Of special interest, however, is the emission centered near 500 nm which persists to many tens of microseconds after excitation. This emission has been observed in previous studies[9] of PVCz solid films and of NEC in inert polymer matrices. It has been attributed to the triplet excimer of the carbazolyl chromophore and is so assigned in this spectrum.

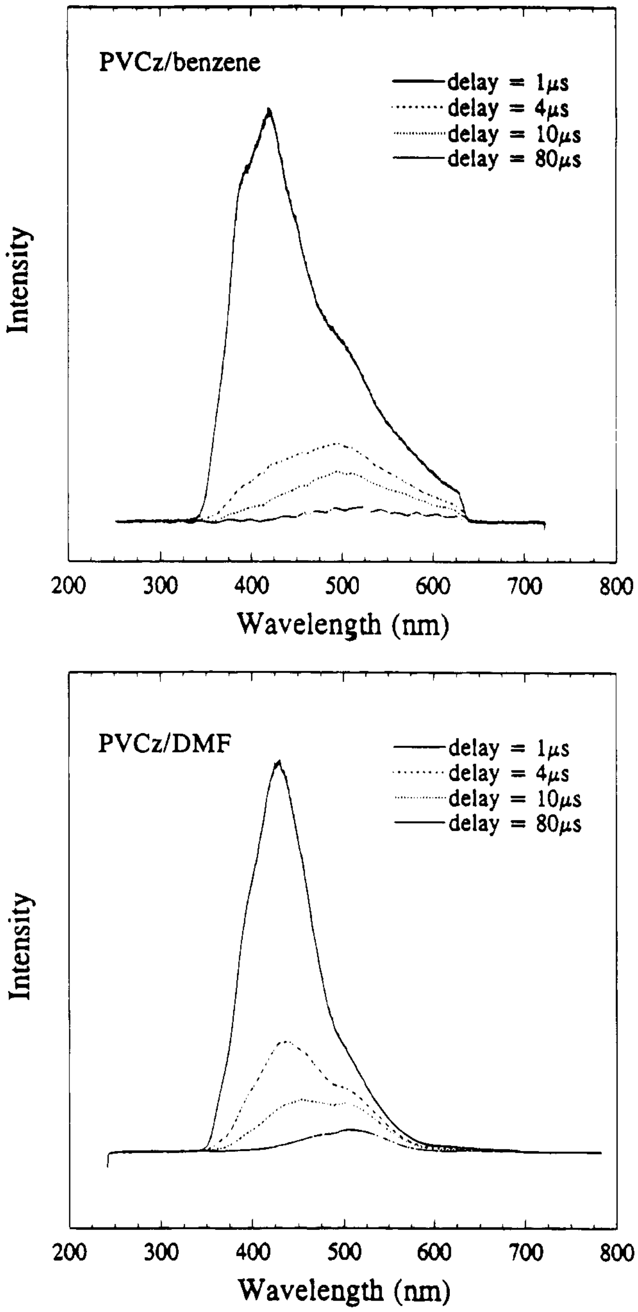

Figure 3. Delayed emission spectra of PVCz in benzene (upper) and DMF (lower) using various delay times and a 6 ms gate.

B. Transient Absorption Spectra. Time-resolved transient absorption spectra of degassed solutions of DCP in benzene, cyclohexane, and DMF are presented in Figure 4. In cyclohexane the spectrum is essentially identical to that found earlier[5] for NEC in this solvent. That is, it consists of a single band at 420 nm which is assigned to the triplet–triplet absorption. In benzene the maximum also occurs at 420 nm, but the band is broader than in cyclohexane. No absorption bands which could be attributed either to the radical cation or the radical anion were found in cyclohexane or

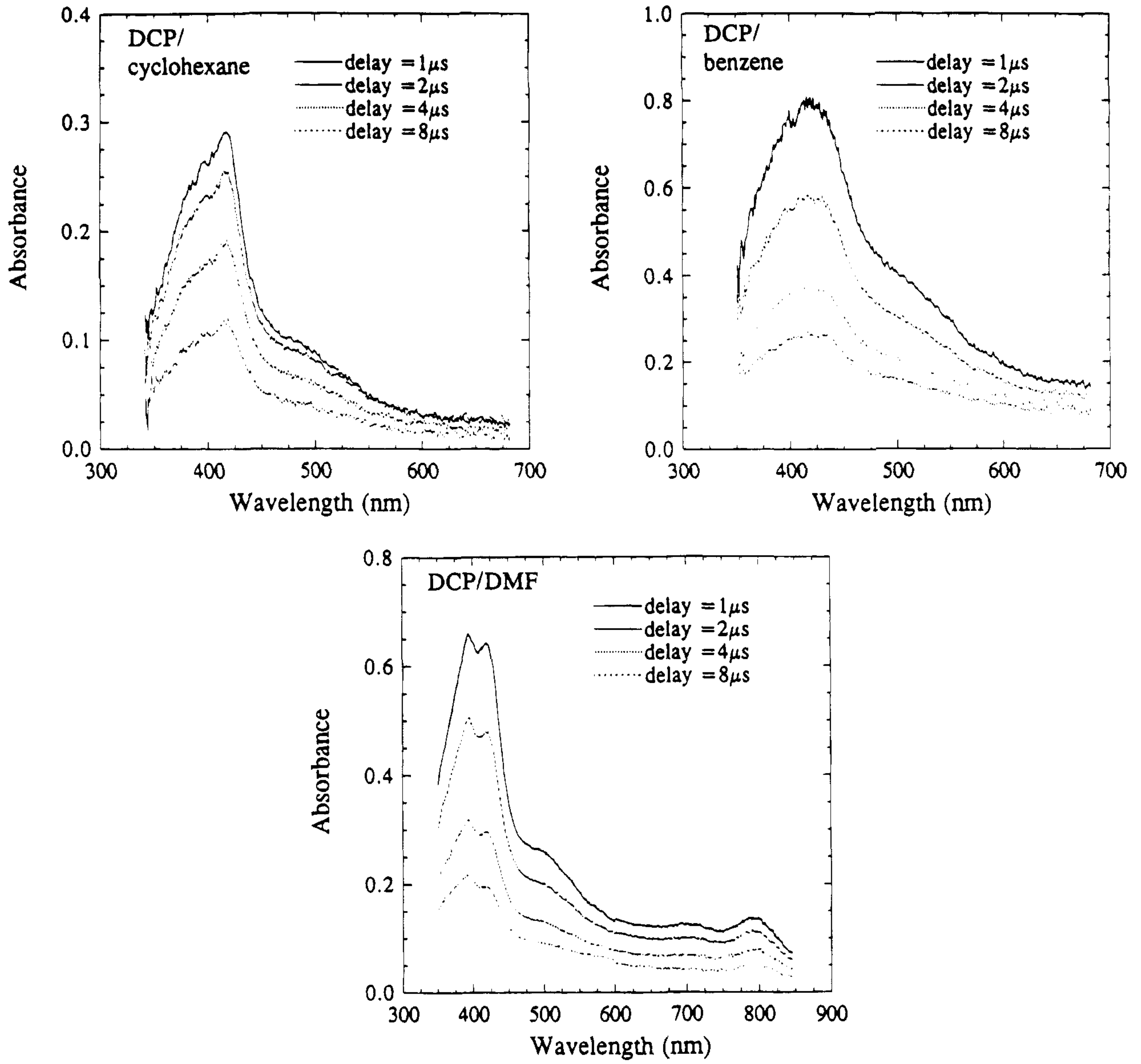

Figure 4. Transient absorption spectra of DCP in cyclohexane (upper left), benzene (upper right), and DMF (lower) at various delay times using a 1 μs gate.

benzene solutions. Transient absorption spectra for DCP in DMF contain several bands including low-wavelength components near 390 and 420 nm corresponding to the radical anion and the triplet state, respectively, in accordance with earlier assignments for NEC.[4,14] The absorption feature near 790 nm is attributed to the radical cation of the carbazole group, also in accord with earlier work.[2]

Transient absorption spectra for PVCz in benzene and DMF are presented in Figure 5. In order to obtain useful information from these spectra, time delays had to be much shorter than those used for DCP solutions. Notice, for example, that in Figure 5 (upper) where benzene is the solvent well-resolved distinct bands near 430 and 400 nm are found using a delay time of 50 ns, but after 1.7 μs the 400 nm band has become obscured. In accord with earlier assignments[5,14] made using frozen solutions of PVCz and fluid solutions of NEC, the feature at 430 nm is assigned to the monomeric triplet of the carbazolyl chromophore and the feature at 400 nm to the carbazolyl anion. Additionally, the poorly resolved band appearing near 500 nm is assigned to the triplet excimer in accordance with the assignment proposed[1] for a similar feature in spectra of NEC in DMF solutions.

The transient absorption spectra for PVCz in DMF seen in Figure 5 (lower) are more difficult to interpret. Based on previous assignments the predominant absorbance is due to the carbazolyl anion and the triplet excimer with only a small contribution from the monomer triplet.

C. Kinetics of Luminescent Decay. The kinetics of the luminescence decay of PVCz in benzene were investigated at several different monitoring wavelengths. When care was taken to emphasize the long time tail of these luminescence decays by using a 10 μs delay time and 50 ns per point, the data were well accommodated by a single exponential. Rate constants obtained in this way were 7.9 (±0.8) × 10^4 s^{-1} at 500 nm (triplet excimer) and 1.4 (±0.1) × 10^5 s^{-1} at 365 nm (monomeric DF). At 420 nm where EDF is expected to emit, the long time single-exponential decay was 9.4 (±0.9) × 10^4 s^{-1}, within experimental error the same as that of the triplet excimer and monomeric delayed fluorescence.

The luminescence decays of DCP in cyclohexane and degassed benzene solutions were evaluated at 420 nm corresponding to the peak of the EDF band. Using a laser intensity of 7 mJ/cm^2 and examining the tail of the decay after 25 μs, the data from the cyclohexane

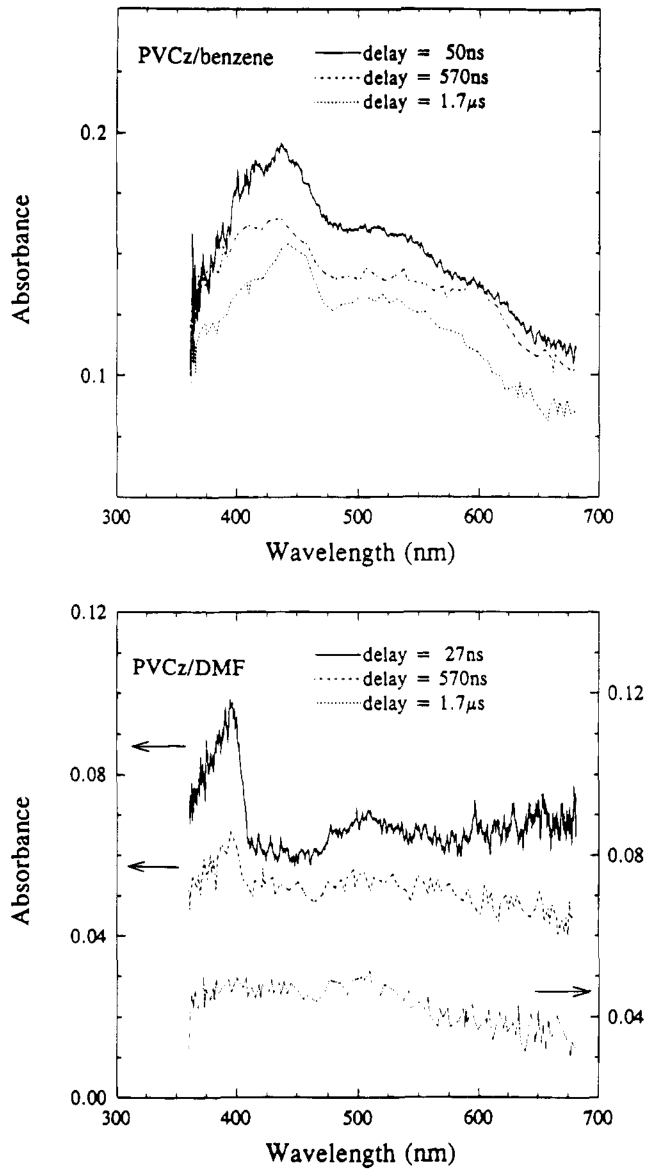

Figure 5. Transient absorption spectra of PVCz in benzene (upper) and DMF (lower) using various delay times and a 280 ns gate.

solutions could be fit to a single-exponential rate law, yielding a rate constant of 2.1 × 10^5 s^{-1}. For the degassed benzene solution a double-exponential yielded a good fit with first-order rate constants of 6.8 × 10^5 and 2.1 × 10^5 s^{-1}. By attenuating the laser pulse 100-fold and examining the tail of the luminescence decay, a single exponential for the degassed benzene solution was found with a rate constant of 1.9 × 10^5 s^{-1} in good agreement with the slow component of the double exponential and the rate constant for the cyclohexane solution. For purposes of comparison with transient absorption results to be presented below, we will assign a value of 2.0 (±0.1) × 10^5 s^{-1} to the rate constant for EDF decay for DCP in benzene and cyclohexane, assuming no contribution from phosphorescence. The luminescence decay for DCP in a degassed DMF solution was also carried out for the EDF band at reduced laser intensity and found to fit a first-order decay with a rate constant of 1.6 (±0.1) × 10^5 s^{-1}.

D. Kinetics of Transient Absorption Decay. The decay of the transient absorbance measured at 430 nm was determined for PVCz in DMF and benzene. This wavelength was chosen because it is well removed from contaminating absorption due to the $^2Cz^-$, and so a reasonably pure absorption due to transient triplets was found. The experimental data fit a pure exponential decay with a χ^2 value of 0.8, but the signal to noise level for these experiments is much smaller than that for DCP as a result of the much reduced absorbance found with the polymer sample in the microsecond time range. Similar agreement was obtained using benzene as the solvent, and the best fit rate constants for these two solvents are 3.8 × 10^4 s^{-1} (DMF) and 3.9 × 10^4 s^{-1} (benzene).

The transient decays corresponding to $^2Cz^+$ and $^2Cz^-$ were determined for PVCz in DMF. A number of different rate laws were tested for these data, but only a double-exponential decay yielded reasonable results. For the cation the best fit gave k_{f+} = 2.4 × 10^6 s^{-1} and k_{s+} = 1.0 × 10^5 s^{-1} where the subscripts f and s refer to fast and slow components, respectively, and the plus sign indicates the cation. The analogous rate constants for the anion are k_{f-} = 2.7 × 10^6 s^{-1} and k_{s-} = 6.2 × 10^4 s^{-1}.

Transient decays for the triplet state of DCP in cyclohexane were monitored at 420 nm and were found to fit a concurrent first- and second-order process. A typical example of the decay data and the fit is found in Figure 6. The triplet decay for DCP in benzene could not be simulated by a concurrent first- and second-order rate law, but the long time tail of the data could be fit by a single exponential, yielding a rate constant of 2.1 (±0.03) × 10^5 s^{-1}.

For DCP in benzene, cyclohexane, and DMF it was possible to test the relationship between triplet concentration and EDF intensity by recording transient decays of each signal under identical conditions and then preparing graphs of EDF intensity versus $[\text{triplet}]^n$. In fact, it is more convenient to use triplet absorbance rather than the triplet concentration itself. Such a graph, for DCP in cyclohexane, is presented here as Figure 7 for n = 2. Similar data were found using benzene as the solvent, and by varying n somewhat and using fractional values, it was found that the best straight line is found for n = 1.8. If the delayed fluorescence arises exclusively by triplet–triplet annihilation and if triplet decay is rigorously exponential, then an n value of 2.0 is expected. When a similar experiment was carried out for DCP in DMF, a linear graph could be obtained only for n = 1.5.

The transient absorption decays for DCP in DMF were evaluated at wavelengths of 380, 420, 550, and 790 nm. Again, by attenuating the laser pulse and emphasizing the long time tail of the decay, it was possible to fit the data for each of these wavelengths to a single-exponential decay. The rate constants are 1.4 × 10^5 (380 nm), 1.1 × 10^5 (420 nm), 1.8 × 10^5 (550 nm), and 2.3 × 10^5 s^{-1} (790 nm). All of these rate data are summarized in Table 1.

Discussion

The delayed emission spectra from DCP in benzene, cyclohexane, and DMF consist primarily of EDF with small contributions from monomeric delayed fluorescence. Furthermore, as expected for the *meso* isomer of DCP, the EDF is centered at 420 nm corresponding to the sandwich excimer structure.

The fact that no sign of any wavelength shift with increasing decay time is found for dilute cyclohexane, benzene, or DMF solutions of DCP is a strong indication that the intramolecular triplet excimer does not form with this molecule. Furthermore, transient absorption

Table 1. Results of Kinetic Decays Measured Either by Luminescence or Transient Absorption for PVCz and DCP

sample	solvent	L[a]:TA[a]/nm	L k_{1s}/s^{-1} [b]	L k_{1f}/s^{-1} [c]	TA k_{1s}/s^{-1} [b]	TA k_{1f}/s^{-1} [c]	TA k_2/M^{-1} [d]
PVCz	benzene	365	1.4×10^4				
PVCz	benzene	420:430	9.4×10^4		3.9×10^4		
PVCz	benzene	500	7.9×10^4				
PVCz	DMF	365:380	7.6×10^5		6.2×10^4	2.7×10^6	
PVCz	DMF	420:430	7.5×10^5		3.8×10^4		
PVCz	DMF	500:780	5.3×10^4		1.0×10^5	2.4×10^6	
DCP[e]	benzene	360	9.1×10^4				
DCP[e]	benzene	420:420	8.7×10^4		6.5×10^4		
DCP	benzene	420:420	2.1×10^5	6.8×10^5	2.1×10^5		
DCP	benzene	420	1.9×10^5				
DCP	cyclohexane	365:420	2.3×10^5		4.4×10^4		4.7×10^9
DCP	cyclohexane	420:500	2.1×10^5		4.6×10^4		5.6×10^9
DCP	DMF	420:380	1.6×10^5		1.4×10^5		
DCP	DMF	–:420			1.1×10^5		
DCP	DMF	–:550			1.8×10^5		
DCP	DMF	–:780			2.3×10^5		

[a] TA indicates a transient absorption experiment; L is luminescence and the value is the wavelength. [b] Best fit for a single-exponential decay. [c] k_f is the fast component for a double-exponential decay; k_s is the slow component. [d] Best fit for concurrent first- and second-order process. Molar absorptivities of 13 500 and 420 nm and 4000 for 510 nm were assumed for the carbazolyl triplet.[15] [e] Indicates DCP conc. = 1.2×10^4 M; others are 8.5×10^{-4} M.

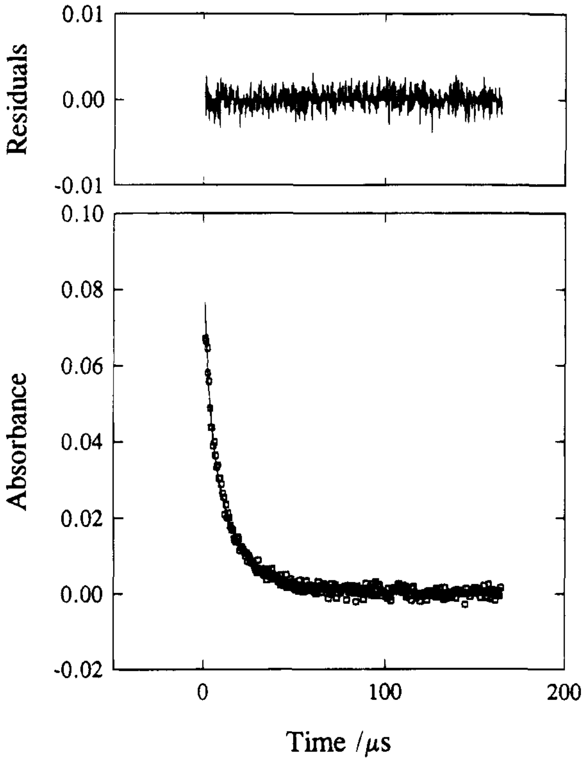

Figure 6. Transient absorption decay of DCP in cyclohexane at 420 nm. The solid line is the best fit to a concurrent first- and second-order decay. Only 10% of the data points are shown for clarity.

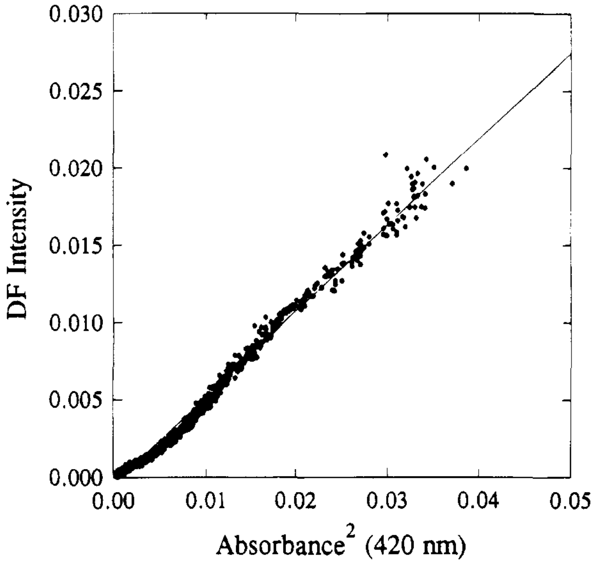

Figure 7. Delayed excimer fluorescence intensity at 420 nm versus the square of the absorbance at 420 nm for DCP in cyclohexane.

spectra for *meso*-DCP in cyclohexane, benzene, and DMF show no indication of a resolved band near 500–550 nm which, in earlier work,[1] has been associated with the carbazole triplet excimer. Further, the transient absorbance decays at 420 nm and the 500–550 nm region fit the same kinetic model with similar decay rates for both DMF and cyclohexane solutions (see Table 1). Clearly, a ground-state chromophore is present as a nearest neighbor to any triplet chromophore produced in this molecule, yet there is no emission and there is no transient absorption attributable to triplet excimers. Models of *meso*-DCP clearly indicate that a face-to-face type of sandwich arrangement between the intramolecular chromophores is a low-energy conformation for this molecule. One is forced to conclude, therefore, that the sandwich geometry is not favorable for the formation of triplet excimers of the carbazole group. It is worth noting that upon increasing the concentration of DCP in DMF the possibility of intermolecular triplet excimer formation arises. Evidence for this can be seen in the long delay time spectra of a concentrated solution of DCP in DMF where the center band shifts to the red (see Figure 2). This emission probably consists of EDF and excimeric phosphorescence since the band does not shift as far as 500 nm, the normal emission maximum for excimeric phosphorescence.

The mechanism of delayed fluorescence formation in these bichromophoric molecules is of some interest. The conventional mechanism would include a triplet–triplet annihilation event to form an excited singlet state and a ground-state chromophore. The excited singlet state would then be expected either to relax directly by a radiative or nonradiative process or else to interact with a neighboring chromophore to form an intramolecular singlet excimer. The formation of an intermolecular excimer might also take place, but its rate would probably be considerably less than that of the intramolecular process. The triplet–triplet annihilation mechanism for EDF formation in benzene and cyclohexane solutions is supported by the results presented in Figure 6. This plot shows that the EDF intensity is proportional to the square of the triplet absorbance.

When DMF is used as the solvent, the transient absorption spectra and the decay kinetics of DCP become much more complicated than in cyclohexane. As indicated above, transient absorption signals for the radical anion near 390 nm and for the radical cation near 790 nm are found in DMF in addition to that for the carbazole triplet state at 420 nm. In general, both luminescence decays and transient absorption decays are about an order of magnitude faster in DMF than in benzene. The absorption bands for the triplet and for the radical anion overlap considerably, and so the transient absorption decays at their peak wavelengths do not correspond to decays of the pure species. We find decay rate constants of 1.1×10^5 and 1.4×10^5 s^{-1} at the wavelength maxima for the triplet and the anion, respectively. For the radical cation at 790 nm there are no other nearby absorptions, and we find a decay rate constant of 2.3×10^5 s^{-1} for this species. The EDF decay at 420 nm proceeds with a first-order rate constant of 1.6×10^5 s^{-1}. When the EDF intensity is graphed versus $[\text{triplet}]^n$, a straight line is found for $n = 1.5$ and so we conclude that triplet–triplet annihilation makes a contribution to EDF production but one or more additional sources must also be considered. Our earlier work[5] on NEC provides a basis for suggesting that EDF could arise by ion recombination between a cation or a cation dimer and an anion.

The spectroscopic and kinetic results for PVCz solutions provide additional useful insights about the fate of these excited states. One of the most significant is the appearance of excimeric phosphorescence from photoexcited benzene solutions. It is possible that ion recombination leads to the production of triplet excimers since the anion is present at short times after the laser pulse, but it is also likely that these excimers are formed by the simple interaction of a monomeric triplet with a nearby ground-state species. The exact mechanism for triplet excimer production has not been determined in this study, but it is most likely a combination of both routes. The fact that intramolecular triplet excimers are present in PVCz and not in DCP was, at first, surprising. However, in view of the large density of ground-state chromophores in the immediate vicinity of any electronically excited chromophore, efficient energy migration of the excited state is possible, and due to the large number of internal degrees of rotational freedom for the polymer, it is expected that partners suitably oriented for excimer formation might be abundant.

Finally, in DMF solutions of PVCz the delayed excimer fluorescence decays at a faster rate (7.5×10^5 s^{-1}) than found in the benzene solution (9.4×10^4 s^{-1}). This faster rate can not be accounted for by differing rates of triplet decay since these rate constants are nearly identical in the two solvents (3.8×10^4 s^{-1}). Therefore, one is forced to conclude that delayed excimer fluorescence must be, in part, produced by ion recombination. In a previous report[5] it was shown for NEC in DMF solutions that ion recombination was the major contributor to the production of delayed fluorescence. In the case of PVCz it is most likely a combination of both triplet–triplet annihilation and ion recombination that leads to the production of delayed fluorescence.

Conclusions

Triplet photophysical processes in multichromophoric molecules have several distinctive characteristics compared with monochromophoric molecules. At low temperatures in a rigid glassy medium the phosphorescence emission from DCP is essentially identical to that of NEC, indicating no intrachromophore interaction under these conditions. In fluid solutions at ambient temperature, again there is no indication of triplet chromophores interacting with their intramolecular neighbors. The kinetics of triplet decay, delayed fluorescence decay, and the dependence of delayed fluorescence intensity upon triplet concentration all point to a remarkable degree of independent behavior for the two carbazolyl groups of *meso*-DCP. From these results, the additional conclusion may be drawn that, for the carbazolyl chromophore, triplet–triplet interactions and triplet–ground state interactions are strongly influenced by relative geometrical orientations of the two chromophores. On the other hand, the fact that intramolecular chromophore pairs are situated in close proximity seems to be relatively unimportant. The results for triplet-state spectroscopy and excited-state decay kinetics of PVCz are readily understandable in this same context since relative geometrical orientations between chromophore pairs span a much wider range of possible geometrical orientations. This is true since chromophore pairs are not necessarily backbone neighbors. They may, for example, arise from the interaction of chain segments coiling back into close proximity with segments far removed as measured along the chain contour. Thus, intramolecular triplet excimer formation is to be expected for PVCz in the absence of ion formation. The experimental results are in accord with this model.

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