

**PHOTOPHYSICS OF PHOTOCONDUCTING POLYMERS WITH  
PENDANT BICHROMOPHORES  
I: INTRAMOLECULAR PHOTOPROCESSES IN 9-[ $\gamma$ -(*N*-  
CARBAZOLYL)PROPYL]-9-METHYL-2,7-DINITROFLUORENE**

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**Summary**

Electronic absorption and luminescence spectroscopies were used to study the intramolecular photoprocesses in the bichromophoric D-A compound 9-[ $\gamma$ -(*N*-carbazolyl)propyl]-9-methyl-2,7-dinitrofluorene (II) together with the monochromophoric model molecules *N*-ethylcarbazole (NEC) and 9- $\gamma$ -hydroxypropyl-9-methyl-2,7-dinitrofluorene (I). It was shown that no intramolecular charge transfer interaction exists between the carbazolyl and the 2,7-dinitrofluorene chromophores in the electronic ground state of the bichromophoric compound II in EPA at room temperature and at 77 K. In contrast, the strong quenching effect of the fluorescence and phosphorescence emission of the carbazolyl chromophore in the bichromophoric molecule II was explained in terms of intramolecular energy transfer and the possible electron transfer interactions between the carbazolyl and the 2,7-dinitrofluorene groups. These two intramolecular photoprocesses in II were characterized well by the Förster critical transfer distance ( $R_0 = 28.6 \text{ \AA}$  at 296 K and  $R_0 = 30.4 \text{ \AA}$  at 77 K) and by the Rehm-Weller free energy change of the electron transfer step ( $\Delta G_{ET} < 0$ ) respectively. Electron transfer processes are usually facilitated by good orbital overlap, but this is not favored by the spatial conformation of the chromophores in II. This is in agreement with the fact that the phosphorescence lifetime ( $\tau_P = 0.12 \pm 0.01$ ) and the phosphorescence quantum yield ( $\phi_P = 0.060 \pm 0.006$ ) of the monochromophoric molecule I remain the same in II and in the polymer (III) (polysebacate containing II as a pendant group). We concluded that long-range energy transfer (Förster type) seems to be the dominant path in these systems.

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## 1. Introduction

Carbazole-based polymers have been the object of extensive studies in recent years in view of the fact that the carbazolyl chromophore has yielded the best photoconducting polymer, the 2,4,7-trinitrofluorenone (TNF) doped poly(*N*-vinylcarbazole) (PNVC) [1]. The spectroscopy and photophysics of a large number of carbazoles [2 - 5] and dicarbazolyl compounds [6 - 10] led many investigators to study the complexities of the photophysical processes of PNVC. Among other photoprocesses, PNVC shows very efficient excimer formation and excitation migration characteristics [11].

Polymers containing the pendant carbazolyl chromophore are good electron donors. They form charge transfer complexes with a number of strong organic electron acceptor molecules [1, 12 - 14] such as tetracyanoquinodimethane (TCNQ), tetracyanoethylene (TCNE) and TNF. The well-defined charge transfer electronic transitions in the visible part of the spectrum significantly lower the excitation energy of the polymers, enhancing and modifying their electrical and photoelectrical properties. The role played by charge transfer interactions in the PNVC-TNF system is undoubtedly responsible for its being known as the best photoconducting polymeric material [14, 15].

Carbazole and its *N*-substituted derivatives (electron donors, D) and, among others, fluorene and its nitro- and cyano-substituted derivatives (electron acceptors, A) are expected to be effective systems of the D-spacer-A type which could be used to generate polymers possessing special photoconducting properties. The photoconducting properties of such polymers could be modified on the basis of the relative electron donor-electron acceptor properties of the chromophores linked by UV-transparent spacers as well as by variation of the distance between the bichromophoric pendant groups in the polymer. Taking into consideration the spectroscopic and photophysical properties of the bichromophores in relation to the photoconductivity of the corresponding polymer, we have chosen 9-[ $\gamma$ -(*N*-carbazolyl)propyl]-9-methyl-2,7-dinitrofluorene as a first model compound in our study of a series of bichromophoric molecules. In this work, the intramolecular photoprocesses of the model bichromophoric molecule was studied on the basis of the luminescence properties of the chromophores. The possibility of intramolecular energy transfer and electron transfer taking place between the chromophores in the bichromophoric molecule will be the object of discussion.

We have shown that when the carbazolyl chromophore is in its first excited singlet electronic state energy transfer dominates over electron transfer which is an equally favored process. However, when the 2,7-dinitrofluorene chromophore is in its excited singlet electronic state, intramolecular electron transfer in the bichromophoric molecule does not occur because of a highly efficient intersystem crossing process due to the nitro groups and/or because of a very weak overlap between the orbitals of both chromophores

involved in the bichromophore. Both processes, intramolecular energy and electron transfer, seem to be dependent on the spatial conformation of the chromophores in the bichromophoric molecular system.

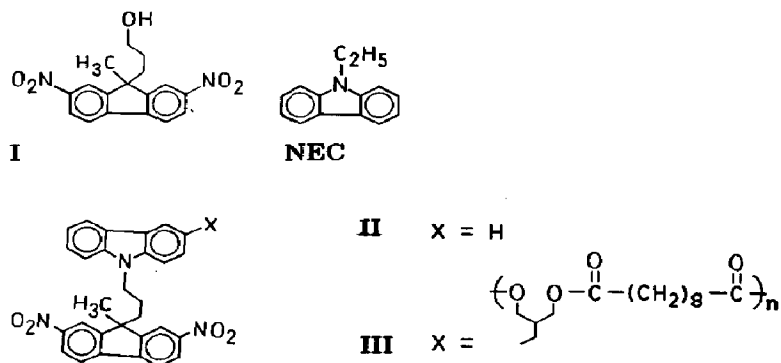
## 2. Experimental details

### 2.1. Materials

*N*-Ethylcarbazole (NEC) (purity, 99%) was obtained from Aldrich Chemical Co. and was further recrystallized twice in pure ethanol and then purified by column chromatography with silica gel using a petroleum ether-ethyl ether mixture (1000:1 by volume) as a developing system.

9- $\gamma$ -Hydroxypropyl-9-methyl-2,7-dinitrofluorene (I) and 9- $\gamma$ -(*N*-carbazolyl)propyl-9-methyl-2,7-dinitrofluorene (II) were synthesized and purified as described previously [15]. The polysebacate (III) containing the bichromophoric molecule II as a pendant group was synthesized and purified as described in another paper [16].

The structural formulae of the compounds studied are as follows:



Spectrophotometric grade acetonitrile (purity, 99%) was obtained from Aldrich Chemical Co. and was distilled before use.

Isopentane, of pure grade quality from Phillips Petroleum Co. and ethyl ether, an analyzed reagent from Baker, were purified in the same way as 3-methylpentane (3MP) (see ref. 17).

Petroleum ether, 35 - 60 °C, an analyzed reagent from Baker, was distilled before use.

Ethanol was purified by refluxing with concentrated sulfuric acid (4 ml H<sub>2</sub>SO<sub>4</sub> in 1000 ml solvent) for 24 h and then was distilled twice before use.

The EPA mixture solvent was made from ethyl ether, isopentane and ethanol in the volume ratio of 5:5:2 respectively.

### 2.2. Apparatus

Absorption spectra were recorded by means of a Cary-17 spectrophotometer using 1.0 and 1.3 cm quartz cells. The low temperature Dewar

including a 1.3 cm quartz cell was designed and built in our laboratory. Liquid nitrogen was used at 77 K. Fluorescence and phosphorescence spectra together with fluorescence excitation and phosphorescence excitation spectra were recorded on a Spex Fluorolog fluorometer model 1902, using a cylindrical Dewar assembly. Phosphorescence lifetimes were measured by means of a Spex Fluorolog equipped with a model 1934 digital phosphorimeter. The system was checked using the phosphorescence lifetime of europium chloride ( $\text{EuCl}_3 \cdot 6\text{H}_2\text{O}$ , 3.665 g in 10 ml 1 M HCl) at  $\lambda_{\text{exc}} = 395 \text{ nm}$ , which is 0.119 ms [18].

Relative fluorescence and phosphorescence quantum yields were measured and automatically calculated by means of a Nova 3/12 mini-computer, using a FORTRAN program called PHIREND, coupled to the Spex Fluorolog. 9,10-Diphenylanthracene was used as the fluorescence quantum yield standard. In order to check the automated system, the fluorescence and the phosphorescence quantum yields of carbazole in an EPA glass [19] and of *N*-ethylcarbazole in an ethanol glass [20] were reproduced.

Electrochemical reduction potential measurements were made using an EG and G Princeton Applied Research model 264 polarographic analyzer-stripping voltammeter. The current-voltage curves were recorded on a 7005 B X-Y recorder (Hewlett-Packard). The experiments were performed using an EG and G PARC model 303 static mercury drop electrode assembly. The system was equipped with a hanging-mercury-drop working electrode, an aqueous Ag/AgCl, saturated KCl reference electrode and a platinum wire auxiliary electrode. A 0.1 M solution of tetraethylammonium perchlorate (TEAP) in acetonitrile was used as the supporting electrolyte.  $10^{-4}$  M solutions of the electron acceptor compounds were deaerated using dry nitrogen gas and reductions were carried out under a nitrogen atmosphere.

### 3. Results and discussion

#### 3.1. Absorption spectra of the bichromophoric compound II

Figure 1 shows the absorption spectrum of the bichromophoric compound II in EPA solution at room temperature and compares it with the sum of the absorption spectra of the monochromophoric compounds I and NEC. Such a comparison of the absorption spectra clearly shows that no ground state intramolecular charge transfer interaction takes place in the bichromophoric molecule II. A similar conclusion has also been previously reached [17] for the bichromophoric molecule II in a non-polar solvent (3-methylpentane) and also in a polar solvent (acetonitrile). In EPA as in 3-methylpentane there is no exact superposition between the sum of the absorption spectra of I and NEC and the absorption spectrum of II. This indicates a small perturbation between the two chromophores in the bichromophoric system which can only be seen in non-polar or weakly polar

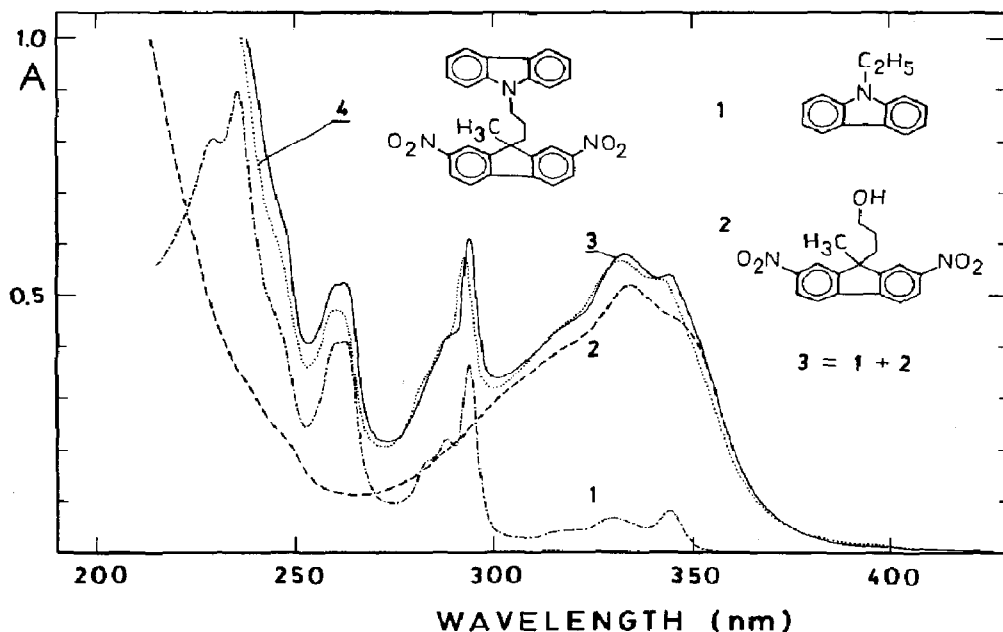


Fig. 1. Electronic absorption spectra of *N*-ethylcarbazole ( $C = 2 \times 10^{-5}$  M,  $l = 1$  cm) (curve 1), 9-( $\gamma$ -hydroxypropyl)-9-methyl-2,7-dinitrofluorene (I) ( $C = 1 \times 10^{-5}$  M,  $l = 1$  cm,  $\times 2$ ) (curve 2) and the sum of the absorption spectra 1 and 2 (curve 3) compared with the electronic absorption spectra of 9-[ $\gamma$ -(*N*-carbazolyl)propyl]-9-methyl-2,7-dinitrofluorene (II) ( $C = 1 \times 10^{-5}$  M,  $l = 1$  cm,  $\times 2$ ) (curve 4) in EPA at 296 K.

solvents. The exact superposition of these spectra was observed in acetonitrile. Figure 2 shows the 77 K absorption spectra of I, II, III and NEC in EPA. The vibrational fine structure is clearly resolved in the various electronic transitions but here again no charge transfer electronic transition is present in the spectra of II and III.

### 3.2. Luminescence properties of the bichromophoric compound II

Singlet excitation of the NEC molecule in EPA solution at room temperature gives rise to fluorescence only, while at 77 K fluorescence and phosphorescence emissions were observed (Fig. 3). The luminescence properties of carbazoles in EPA solution are well known [19 - 22]. The reported values of the fluorescence quantum yield,  $\phi_F(298 \text{ K}) = 0.42$ , and  $\phi_F(77 \text{ K}) = 0.44$ , as well as the phosphorescence quantum yield,  $\phi_P(77 \text{ K}) = 0.24$ , indicate the efficiency of the radiative processes in the carbazole molecule. However, under the same experimental conditions, fluorescence and phosphorescence emissions of the carbazolyl chromophore in the bichromophoric molecule II or in the polymer III are completely quenched. In contrast, the dinitrofluorene derivative I does not emit any fluorescence. Nevertheless, in EPA at 77 K it possesses a characteristic phosphorescence emission spectrum which remains in both the bichromophoric molecule II and the polymer III. Figure 4 shows this phosphorescence emission for compound II in EPA glass at 77 K.

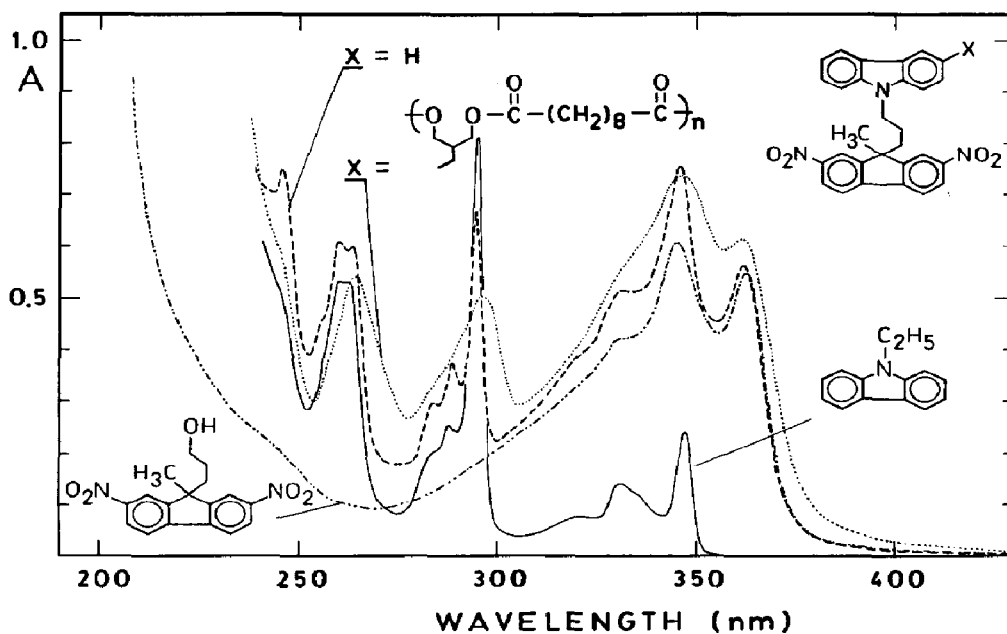


Fig. 2. Electronic absorption spectra of *N*-ethylcarbazole ( $C = 2 \times 10^{-5}$  M,  $l = 1.3$  cm) (—), 9-( $\gamma$ -hydroxypropyl)-9-methyl-2,7-dinitrofluorene (I) ( $C = 1 \times 10^{-5}$  M,  $l = 1.3$  cm) (- · -), 9-[ $\gamma$ -(*N*-carbazolyl)propyl]-9-methyl-2,7-dinitrofluorene (II) ( $C = 1 \times 10^{-5}$  M,  $l = 1.3$  cm) (- - -) and polysebacate (III) ( $C \approx 1 \times 10^{-6}$  M,  $l = 1.3$  cm,  $\times 7.5$ ) (.....) in EPA at 77 K.

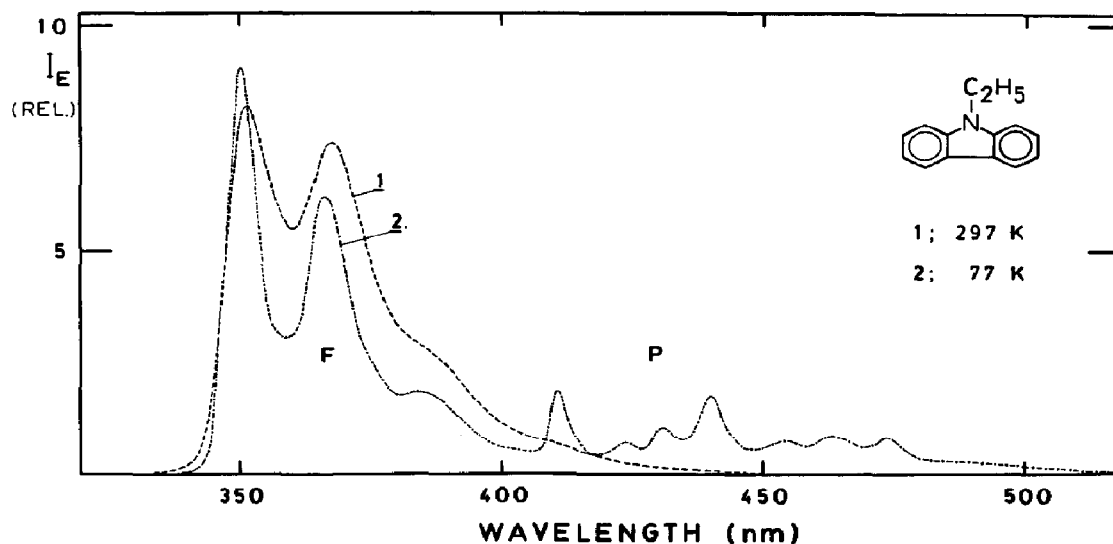


Fig. 3. Emission spectra of *N*-ethylcarbazole ( $C = 1 \times 10^{-5}$  M) at 296 K ( $\lambda_{exc} = 293$  nm) (curve 1) and at 77 K ( $\lambda_{exc} = 295$  nm) (curve 2) in EPA.

In EPA, phosphorescence of the 2,7-dinitrofluorene chromophore in the bichromophoric molecule II and in the polymer III is the only observed emission. Table 1 gives the phosphorescence lifetimes  $\tau_P$  and the

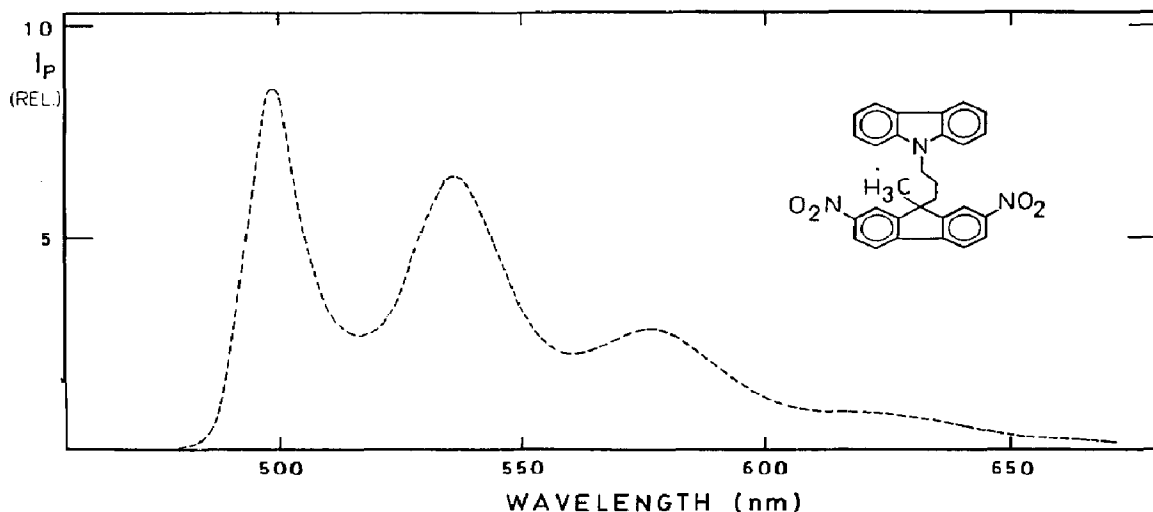


Fig. 4. Phosphorescence spectrum of 9-[ $\gamma$ -(*N*-carbazolyl)propyl]-9-methyl-2,7-dinitrofluorene (II) in EPA ( $C = 1 \times 10^{-5}$  M) at 77 K ( $\lambda_{\text{exc}} = 362$  nm).

TABLE 1

Phosphorescence lifetimes  $\tau_P$  and phosphorescence quantum yields  $\phi_P$  of the 2,7-dinitrofluorene chromophore in molecule I, in bichromophore II and in polymer III (solvent: EPA, 77 K)

Compound	$\lambda_{\text{exc}}$ (nm)	$\tau_P (\pm 0.005)$ (s) at $\lambda_{\text{em}} =$			$\phi_P$
		499 nm	536 nm	580 nm	
I	362	0.119	0.118		$\phi_P(\text{I}) = 0.060 \pm 0.006$
II	362	0.121	0.116	0.125	$\phi_P(\text{II})/\phi_P(\text{I}) = 0.99 \pm 0.05$
	295	0.122			
III	362	0.120	0.121		$\phi_P(\text{III})/\phi_P(\text{I}) = 0.96 \pm 0.05$

phosphorescence quantum yields  $\phi_P$  of these molecular systems in EPA at 77 K and  $\lambda_{\text{exc}} = 362$  nm. The results in Table 1 indicate that the phosphorescence lifetime of the 2,7-dinitrofluorene chromophore in compound I remains the same in the bichromophoric molecule and in the polymer even for excitation of the carbazole moiety (295 nm). The calculated average value is  $\tau_P = 0.12 \pm 0.01$  s. Such a long triplet state lifetime confirms the nature ( $\pi\pi^*$ ) of the phosphorescence transition in these systems. The phosphorescence quantum yields of I, II and III are also the same ( $\phi_P = 0.060 \pm 0.006$ ). The radiative phosphorescence decay rate constant  $k_P$  was calculated as  $k_P = \phi_P/\tau_P = 0.5 \text{ s}^{-1}$  on the assumption that the triplet quantum yield  $\phi_T$  is equal to unity since no fluorescence is observed in these nitro derivatives. The  $k_P$  value thus obtained is also characteristic of a highly forbidden triplet to ground state,  $\pi^* \rightarrow \pi$ , phosphorescence transition.

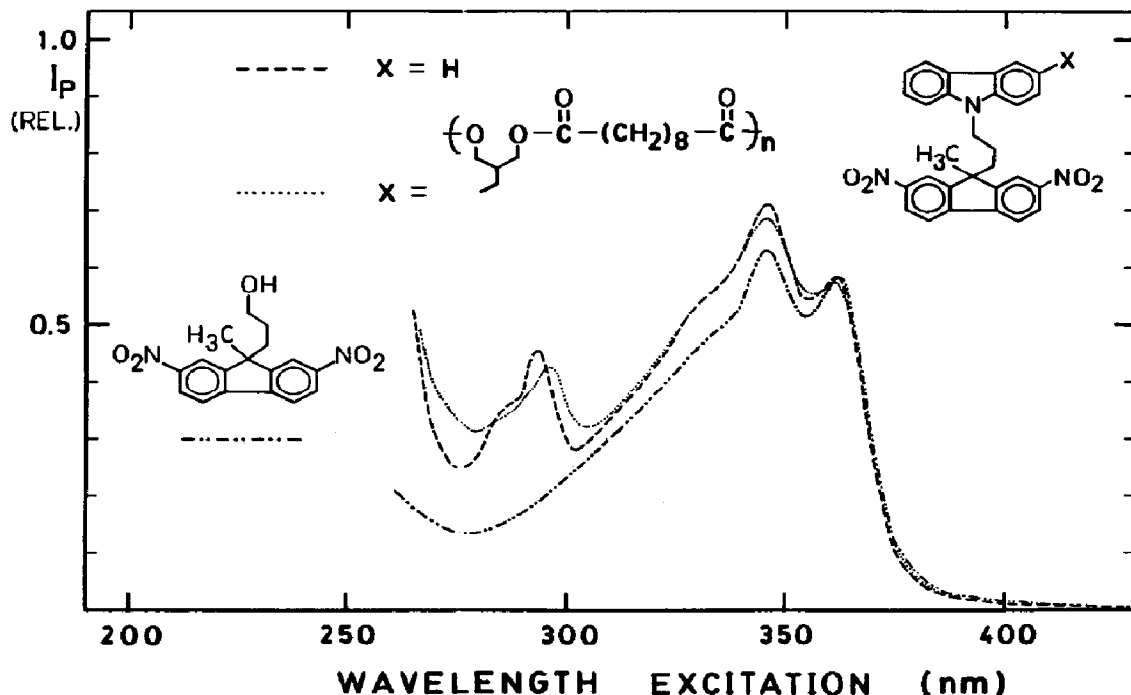


Fig. 5. Phosphorescence excitation spectra of 9-( $\gamma$ -hydroxypropyl)-9-methyl-2,7-dinitrofluorene (I) (— · —), 9-[ $\gamma$ -(*N*-carbazolyl)propyl]-9-methyl-2,7-dinitrofluorene (II) (— — —) and polysebacate (III) (·····) in EPA at 77 K ( $\lambda_{em} = 499$  nm).

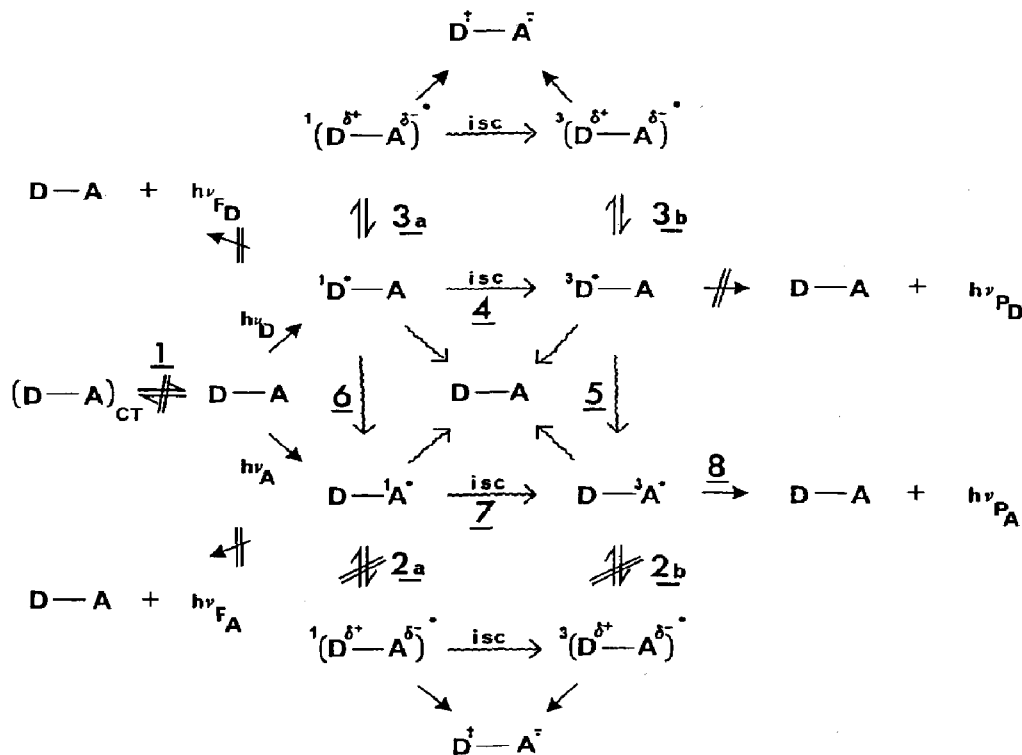
Figure 5 shows the phosphorescence excitation spectra of molecule I, molecule II and polymer III at  $\lambda_{em} = 500$  nm in an EPA glass. The same spectra were also obtained at  $\lambda_{em} = 535$  nm. It is worth noting that at these two emission wavelengths there is no phosphorescence emission from the carbazoyl chromophore (see Fig. 3 (EPA, 77 K)). Nevertheless, the phosphorescence excitation spectra of bichromophore II and polymer III do not correspond to the excitation spectra of molecule I. The phosphorescence excitation spectra of II and III correspond to the absorption spectra of II and III as the phosphorescence excitation spectrum of I corresponds to the absorption spectrum of I (see Fig. 2). Comparing the phosphorescence excitation spectra of the systems studied with their absorption spectra clearly shows the occurrence of energy transfer from the electronically excited carbazoyl chromophore to the 2,7-dinitrofluorene chromophore in the bichromophoric molecular systems since there is no phosphorescence from the carbazoyl moiety. However, following the electronic excitation of the carbazoyl chromophore or the 2,7-dinitrofluorene chromophore in the bichromophoric molecule II or polymer III, no new "intramolecular exciplex" or complex emission is observed at room temperature or at 77 K in the low temperature matrix. Such electron transfer interactions (the formation of an exciplex) might be expected, considering the electron donor-acceptor properties of the two moieties connected by a propylene



bridge. Both phenomena, intramolecular energy transfer and intramolecular electron transfer, are expected to be in competition with each other and this will now be discussed.

### 3.3. Intramolecular photoprocesses in the bichromophoric molecule II

Figure 6 shows the energy level diagram for *N*-ethylcarbazole and molecule I based on their absorption and luminescence spectra in EPA at 77 K. Data on the vibronic transition energies of these compounds presented in Tables 2 and 3 indicate that the corresponding energy levels for NEC and for I do not change significantly in the bichromophore II and in the polymer III. However, it is clear that the first singlet and triplet energy levels of NEC are higher in energy than those of molecule I.  $T_1$  for NEC is  $4330\text{ cm}^{-1}$  (0.56 eV) higher than  $T_1$  for I and  $S_1$  for NEC is  $1230\text{ cm}^{-1}$  (0.15 eV) higher than  $S_1$  for I. This diagram together with the well-known electron donor properties of the carbazolyl chromophore suggest at least two pathways for the photoprocesses in the bichromophoric system: electron and/or energy transfer from the carbazolyl chromophore (D) to the 2,7-dinitrofluorene chromophore (A). The general scheme of the various photoprocesses in the bichromophoric molecule II is presented in Scheme 1.



Scheme 1.

As shown in Fig. 1, the absorption spectrum of the D-A bichromophoric molecule II in EPA (as well as in 3MP and  $\text{CH}_3\text{CN}$ ) is similar to the

TABLE 2

Vibronic transition energies of the carbazolyl chromophore in *N*-ethylcarbazole, in bichromophore II and in polymer III observed in the absorption and the luminescence spectra (solvent: EPA, 77 K)

Vibronic transitions	$\tilde{\nu} (\pm 50) (\text{cm}^{-1})$		
	NEC	II	III
$S_0 \rightarrow S_1$			
0 $\rightarrow$ 0	28820		
0 $\rightarrow$ 1	29850		
0 $\rightarrow$ 2	30210		
0 $\rightarrow$ 3	31250		
$S_0 \rightarrow S_2$			
0 $\rightarrow$ 0	33960	33960	33730
0 $\rightarrow$ 1	34780	34780	34480
0 $\rightarrow$ 2	35460	35460	35090
$S_1 \rightarrow S_0$			
0 $\rightarrow$ 0	28570		
0 $\rightarrow$ 1	27320		
0 $\rightarrow$ 2	25970		
$T_1 \rightarrow S_0$			
0 $\rightarrow$ 0	24330		
0 $\rightarrow$ 1	23590		
0 $\rightarrow$ 2	23150		
0 $\rightarrow$ 3	22730		
0 $\rightarrow$ 4	21980		
0 $\rightarrow$ 5	21600		
0 $\rightarrow$ 6	21100		

TABLE 3

Vibronic transition energies of the 2,7-dinitrofluorene chromophore in molecule I, in bichromophore II and in polymer III observed in the absorption and in the phosphorescence spectra (solvent: EPA, 77 K)

Vibronic transitions	$\tilde{\nu} (\pm 50) (\text{cm}^{-1})$		
	I	II	III
$S_0 \rightarrow S_1$			
0 $\rightarrow$ 0	27590	27620	27620
0 $\rightarrow$ 1	28990		
0 $\rightarrow$ 2	30300		
$T_1 \rightarrow S_0$			
0 $\rightarrow$ 0	20040	20040	20040
0 $\rightarrow$ 1	18660	18660	18660
0 $\rightarrow$ 2	17360	17360	17360
0 $\rightarrow$ 3	16100	16100	16100

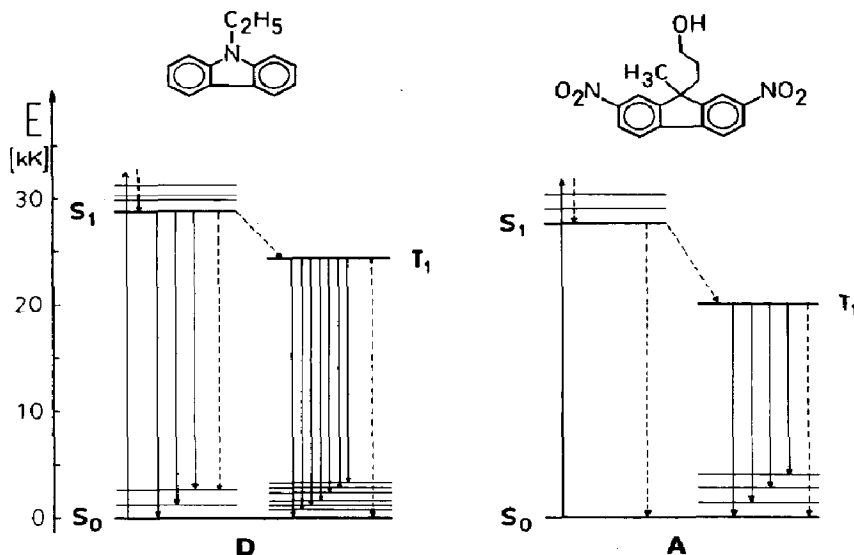


Fig. 6. Energy level diagram for *N*-ethylcarbazole and for 9-( $\gamma$ -hydroxypropyl)-9-methyl-2,7-dinitrofluorene (I) (EPA, 77 K).

sum of the absorption spectra of the monochromophoric molecules I and NEC. This is clear evidence, on the basis of the absorption spectra alone, that no ground state intramolecular charge transfer interactions take place in the bichromophoric molecule. Lack of such interaction in the bichromophoric molecule is indicated in Scheme 1 as process 1. In this scheme  $h\nu_D$  indicates light absorbed by the carbazolyl chromophore (295 nm) and  $h\nu_A$  indicates light absorbed by the 2,7-dinitrofluorene chromophore (295 nm or 362 nm) in the bichromophoric molecule. Scheme 1 also shows that the energy of the singlet electronic excitation in the donor part and/or in the acceptor part of the bichromophoric molecule can be dissipated by radiationless processes such as intersystem crossing (processes 4 and 7), electron transfer (process 3) and  $S_1^D \rightarrow S_1^A$  energy transfer (process 6), since no fluorescence emission was observed for D ( $h\nu_{FD}$ ) or for A ( $h\nu_{FA}$ ) in the bichromophoric molecule II in EPA (or acetonitrile).

Phosphorescence of the 2,7-dinitrofluorene moiety is the only observed emission in the molecular systems (II and III) studied. The first excited triplet state of the 2,7-dinitrofluorene moiety can be formed by processes 7 and 5 as indicated in Scheme 1. Since energy transfer between the 2,7-dinitrofluorene chromophore in its excited electronic states and the carbazolyl ground state chromophore is not energetically feasible (see Fig. 6, endothermic process), electron transfer would be the only feasible mechanism able to quench the observed phosphorescence emission in the bichromophoric compound. Table 1 clearly shows that the phosphorescence lifetimes and the phosphorescence quantum yields are the same in going from molecule I to the bichromophore (II) and to the polymer (III). This

shows that mechanisms 2a and 2b in Scheme 1 are not operative in II and III.

Concerning the intramolecular electron transfer interactions involving the excited carbazolyl chromophore in the first singlet (or triplet) excited state and the 2,7-dinitrofluorene chromophore in the ground electronic state, we do not have any spectral argument either to confirm or to exclude them (mechanisms 3a and 3b). The typical emission of D (see Fig. 6) in the D-A bichromophoric molecule is completely quenched without the appearance of any new emissions which might be ascribed to intramolecular exciplexes. If electron transfer from singlet excited D to A takes place it might give rise to the formation of a non-emissive exciplex,  $^1(D^{\delta+}-A^{\delta-})^*$ , which would only be accessible by the technique of nanosecond or picosecond probing.

In contrast, comparing the phosphorescence excitation spectra of II and III at  $\lambda_{em} = 499$  nm (there is no emission from the carbazolyl chromophore in II or III) with the phosphorescence excitation spectrum of I, and also to the absorption spectra of I, II and III in EPA at 77 K (Figs. 2 and 5) which give rise to the energy level diagram (Fig. 6), clearly shows that energy transfer from the carbazolyl chromophore to the 2,7-dinitrofluorene chromophore is an important interchromophoric photoprocess in II and also in polymer III (5 and 6 in Scheme 1). The intersystem crossing ( $S_1 \rightsquigarrow T_1$ ) quantum yield for carbazole in benzene (energy gap  $S_1-T_1$ ,  $3700\text{ cm}^{-1}$ ) has been measured as  $\phi_{ISC} = 0.36$  [23]. A similar value of  $\phi_{ISC}$  can also be expected for the carbazolyl chromophore in the bichromophoric molecule on the basis of the energy gap alone. If it is assumed that this process is not perturbed by the nitro groups in the fluorene ring or by other intramolecular photoprocesses in the bichromophore, it might be expected that both processes 5 and 6 are effective in these bichromophoric systems.

Nevertheless, the phosphorescence emission observed for NEC in EPA (Fig. 3) is completely quenched in the bichromophoric molecular system. Such efficient quenching of the phosphorescence of the carbazolyl chromophore may be due to  $T_1^D \rightarrow T_1^A$  energy transfer (process 5, Scheme 1) but can be also explained by the low population of the state  $^3D^*-A$ , owing to the efficient quenching of the singlet state of the carbazolyl chromophore by process 6 ( $S_1^D \rightarrow S_1^A$  energy transfer) and by process 3 ( $^1D^*-A \rightarrow ^1[D^{\delta+}-A^{\delta-}]^*$  intramolecular electron transfer).

The state of the bichromophoric molecule denoted  $D-^3A^*$  can be formed through three different pathways. Two of these,  $h\nu_D \rightarrow 6 \rightarrow 7$  and  $h\nu_A \rightarrow 7$ , involve intersystem crossing (process 7) in the acceptor chromophore A, which is clearly indicated by the fact that only phosphorescence has been observed in the 2,7-dinitrofluorene moiety. The other pathway,  $h\nu_D \rightarrow 4 \rightarrow 5$ , is strongly dependent on the intersystem crossing probability (process 4) in the donor chromophore D.

The probability of these various processes for the bichromophoric molecule II will now be discussed on the basis of their rate constants. Energy transfer and electron transfer will first be examined in greater detail.

### 3.3.1. Energy transfer in the D-A system

The existence of partial overlap between the absorption spectrum band of the 2,7-dinitrofluorene chromophore (energy acceptor) and the fluorescence emission band of the carbazolyl chromophore (energy donor) (see Fig. 7) allows us to consider the two different mechanisms of  $S_1^D \rightarrow S_1^A$  energy transfer, radiative and non-radiative.

The efficiency  $\phi_{RT}$  of intramolecular radiative energy transfer when the emitted quantum by the donor chromophore is absorbed by the acceptor chromophore can be estimated from the following expression [24]:

$$\phi_{RT} = \phi_D^0 \frac{3.8 \times 10^{-21} \epsilon_A^{\max}}{4\pi R^2} \quad (1)$$

where  $\phi_D^0$  is the fluorescence quantum yield of the donor in the absence of energy transfer,  $\epsilon_A^{\max}$  ( $M^{-1} \text{ cm}^{-1}$ ) is the extinction coefficient of the acceptor at  $\lambda_{\max}$  and  $R$  is the donor-acceptor separation distance in centimetres. For the bichromophoric molecular system studied in EPA at 77 K the value of  $\phi_{RT}$  can be calculated using  $\phi_D^0 = 0.44$  measured for the carbazole

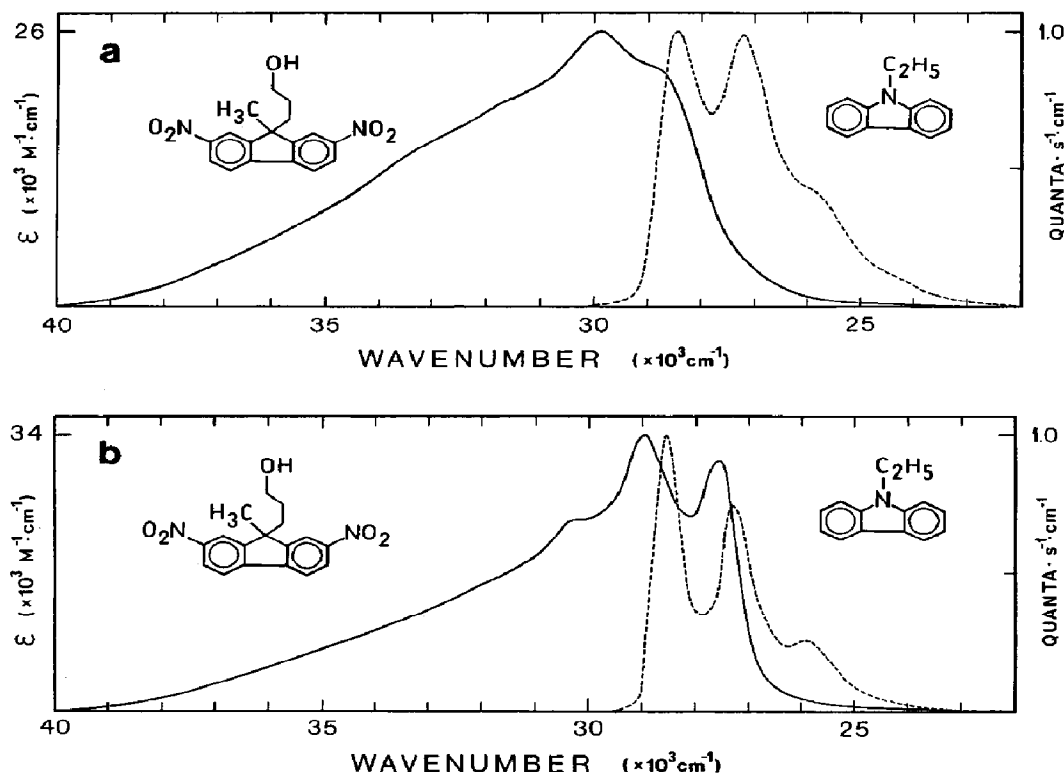


Fig. 7. Long-wave absorption band of 9-( $\gamma$ -hydroxypropyl)-9-methyl-2,7-dinitrofluorene (I) (—) and normalized corrected fluorescence spectrum of *N*-ethylcarbazole (- - -) in EPA (a) at 296 K and (b) at 77 K. The normalization of the fluorescence spectrum was made to show the overlap between the acceptor absorption and the donor emission spectra.

molecule [21],  $\epsilon_A^{\max} = 3.4 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$  (from the absorption spectrum of molecule I in EPA at 77 K) and  $R = 3.75 \text{ \AA}$  (for the sandwich conformation of the chromophores in the bichromophoric molecule II, according to Dreiding models). The value of  $\phi_{RT}^{77\text{K}}$  is 0.0032. In EPA at room temperature  $\phi_D^0 = 0.42$  and  $\epsilon_A^{\max} = 2.6 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ . For the sandwich conformer of II,  $\phi_{RT}^{296\text{K}} = 0.0023$ . These values of  $\phi_{RT}$  are much too small (and would be smaller for the low energy conformation of the bichromophore where  $R = 8.6 \text{ \AA}$  [17]) to explain the observed fluorescence quenching efficiency of the carbazoyl chromophore.

The fluorescence spectrum of NEC ( $2 \times 10^{-6} \text{ M}$ ) in EPA or acetonitrile at room temperature changes only slightly in the presence of I at a concentration of  $2 \times 10^{-6} \text{ M}$ . The fluorescence band intensity of NEC decreases if the concentration of I is increased by a factor of 10 or more. Since, under the same experimental conditions, the fluorescence of the carbazoyl chromophore in the bichromophoric molecule II ( $2 \times 10^{-6} \text{ M}$ ) is completely quenched, it is obvious that this quenching is strongly dependent on the donor-acceptor distance, and this is explained better by the radiationless energy transfer mechanism.

This mechanism can be discussed in two ways: in terms of either long-range dipole-dipole interactions (Förster mechanism) [25] or short-range exchange interactions (Dexter mechanism) [26]. The Förster mechanism is always predominant when the distance between the donor and the acceptor molecules is greater than  $10 \text{ \AA}$ . At shorter distances both mechanisms can play a role. In the Förster mechanism the energy transfer rate constant  $k_{FT}$  is given by the equation

$$k_{FT} = \frac{1}{\tau_D^0} \left( \frac{R_0}{R} \right)^6 \quad (2)$$

where  $\tau_D^0$  is the fluorescence lifetime of the donor molecule and  $R_0$  is the critical transfer distance at which energy transfer and spontaneous decay of the excited donor are equally probable. The critical transfer distance is a term which can also be used to express the theoretical efficiency  $T$  of the Förster-type energy transfer:

$$T = \frac{(R_0/R)^6}{1 + (R_0/R)^6} \quad (3)$$

$R_0$  can be calculated on the basis of spectroscopic data using the following expression:

$$R_0^6 = \frac{9000 \ln 10}{128\pi^5 N_A} \frac{\kappa^2 \phi_D^0}{n^4} I_D^F \quad (4)$$

where  $N_A$  is Avogadro's number,  $\kappa^2$  is a dimensionless orientational factor [27] for the chromophore dipoles,  $n$  is the refractive index of the medium in the overlap region and  $I_D^F$  ( $\text{mmol}^{-1} \text{ cm}^6$ ) refers to the spectral overlap

between the energy donor emission and energy acceptor absorption bands and is defined as

$$I_{\tilde{\nu}}^F = \int_0^{\infty} F_D(\tilde{\nu}) \epsilon_A(\tilde{\nu}) \frac{d\tilde{\nu}}{\tilde{\nu}^4} \quad (4a)$$

where  $\tilde{\nu}$  is the wavenumber in the overlap region,  $\epsilon_A(\tilde{\nu})$  ( $M^{-1} \text{ cm}^{-1}$ ) is the molar decadic extinction coefficient of the acceptor and  $F_D(\tilde{\nu})$  is the spectral distribution of the donor emission in quanta and normalized to unity ( $\int F_D(\tilde{\nu}) d\tilde{\nu} = 1$ ).

The Dexter mechanism of energy transfer can only be efficient when the distance between the donor and the acceptor molecules is shorter than 10 Å. The relevant rate constant ( $k_{DT}$ ) can be described in the form

$$k_{DT} = \frac{4\pi^2}{h} K I_{\tilde{\nu}}^D \exp\left(-\frac{2R}{L}\right) \quad (5)$$

where  $L$  is the average Bohr radius involved in the initial and final states of the system described by the wave functions  $\Psi_i$  and  $\Psi_f$  respectively [28].  $I_{\tilde{\nu}}^D$  is an overlap integral of the type

$$I_{\tilde{\nu}}^D = \int_0^{\infty} F_D(\tilde{\nu}) \epsilon_A(\tilde{\nu}) d\tilde{\nu} \quad (5a)$$

in which  $F_D(\tilde{\nu})$  is the spectral distribution of the donor emission expressed in quanta and  $\epsilon_A(\tilde{\nu})$  is the spectral distribution of the acceptor absorption, each normalized to unity ( $\int F_D(\tilde{\nu}) d\tilde{\nu} = \int \epsilon_A(\tilde{\nu}) d\tilde{\nu} = 1$ ).  $K$  is a constant which is not related to any spectroscopic experimental data and thus, unlike  $R_0$ , has only qualitative value.

Taking into consideration the fact that no ground state intramolecular charge transfer interaction between the donor and the acceptor chromophores in the bichromophoric molecule II have been detected and also the fact that the absorption spectrum of molecule II is the sum of the spectra of NEC and of molecule I, the spectral overlap between the fluorescence band of the carbazolyl chromophore and the absorption band of the 2,7-dinitrofluorene chromophore in molecule II was obtained from the separated monochromophoric molecules, NEC and I.  $I_{\tilde{\nu}}^F$  and  $I_{\tilde{\nu}}^D$  together with  $\phi_D^0$ ,  $\tau_D^0$ ,  $\kappa^2$  and  $n_{EPA}$  at room temperature and at 77 K are presented in Table 4. These data were used to calculate the critical transfer distance from eqn. (4).  $R_0$  values at room temperature (28.6 Å) and at 77 K (30.4 Å) together with the interchromophoric distance,  $R = 8.6$  Å for the low energy conformer of the bichromophore II [17] were used in eqn. (3) to show that the Förster-type energy transfer is highly efficient in the system studied ( $T \approx 100\%$ ). Furthermore, the rates of energy transfer were calculated from eqn. (2).

The spectral overlap expressed as  $I_{\tilde{\nu}}^F$  or  $I_{\tilde{\nu}}^D$  significantly increases in going from room temperature to 77 K (see Table 4). This is due to the

TABLE 4

Photophysical and spectroscopic properties of the bichromophoric molecule II and its monochromophoric model compounds in EPA solution

Temperature (K)	$\phi_D^{0a}$	$\tau_D^{0b}$ ( $s^{-1}$ )	$\kappa^{2c}$	$n_{EPA}$	$I_D^F (I_D^D (cm))^{-1} cm^6$	$R$ (Å)	$R_0$ (Å)	$k_{FT}^{-1}$ ( $s^{-1}$ )	$T$ (%)
296	0.42	$15.5 \times 10^{-9}$	2/3	1.971 <sup>d</sup>	$7.838 \times 10^{-15}$ ( $3.196 \times 10^{-5}$ )	8.6	28.6	$8.7 \times 10^{10}$	99.93
77	0.44	$15.4 \times 10^{-9}$	0.475	1.500 <sup>e</sup>	$21.859 \times 10^{-15}$ ( $7.775 \times 10^{-5}$ )		30.4	$1.3 \times 10^{11}$	99.95

<sup>a</sup>See ref. 21.

<sup>b</sup>See refs. 22 - 24.

<sup>c</sup>See ref. 27.

<sup>d</sup>Obtained for  $\lambda = 350$  nm from the relation  $n_{EPA}^{296} = [1.8083 + (8823.4/\lambda^2)]^{1/2}$  (where  $\lambda$  is in nanometres) derived on the basis of literature data [29].

<sup>e</sup>Obtained for  $\lambda = 357$  nm from the relation  $n = f(1/\lambda^2)^{1/2}$  [30].



red-shifted absorption band of the energy acceptor as well as to the modification of the fluorescence band of the energy donor (increase in the solute-solvent interaction) when the temperature decreases (see Fig. 7). However, this solute-solvent interaction has a minor effect on the energy transfer probability  $k_{\text{ET}}$ .

Considering the large spectral overlap which gives rise to the large value of  $R_0$ , the intermolecular electronic energy transfer from the singlet excited NEC to molecule I as well as the intramolecular electronic energy transfer in the bichromophoric molecule II should involve the dipole-dipole interaction mechanism (Förster type). In the bichromophoric molecule II where the distance between the chromophores is 8.6 Å or less (depending on the conformation of the chromophores in the molecule) the interchromophoric energy transfer process might also involve the Dexter exchange mechanism.

According to the Wigner spin rule [15] the  $S_1^{\text{D}} \rightarrow S_1^{\text{A}}$  energy transfer is allowed for both long-range and short-range mechanisms. The intramolecular  $S_1^{\text{D}} \rightarrow S_1^{\text{A}}$  energy transfer in a series of bichromophoric molecules consisting of cyclic  $\alpha$ -diketones incorporating an ortho-, meta- or para-substituted benzene ring [28] can serve as an example for the Dexter exchange mechanism. In this type of bichromophoric molecule the distances between the donor and the acceptor chromophores separated by methylene chains vary in the range 3.6 - 6 Å. The calculated spectral overlap  $I_{\nu}^{\text{D}}$  between the xylene emission and the biacetyl absorption is  $2 \times 10^{-7}$  cm. However, the critical transfer distance  $R_0$  calculated for this system is 10 Å. These values together with good orbital overlap between the chromophores appear to be consistent with the Dexter mechanism of energy transfer in the bichromophoric system studied [28]. However, these values are much lower than those reported in this paper (see Table 4). The Dexter mechanism, if valid in II, will obviously not contribute much to the energy transfer process in view of the large value of  $R_0$  and also in view of the fact that very weak orbital overlap between the chromophores exists in the low energy conformer of II.

### 3.3.2. Electron transfer in the D-A system

The feasibility of the electron transfer process between donor and acceptor molecules ( $\text{D}^* \cdots \text{A} \rightarrow \text{D}^{\ddagger} + \text{A}^-$ ,  $\text{D} \cdots \text{A}^* \rightarrow \text{D}^{\ddagger} + \text{A}^-$ ) can be measured in terms of the free-energy change  $\Delta G_{\text{ET}}$  of the electron transfer step.

The free-energy change  $\Delta G_{\text{ET}}$  associated with radical ion pair formation can be determined from the well-known Rehm-Weller equation [31]

$$\Delta G_{\text{ET}} = E_{1/2}^{\text{ox}}(\text{D}/\text{D}^{\ddagger}) - E_{1/2}^{\text{red}}(\text{A}^-/\text{A}) - E_{0,0}^* + C \quad (6)$$

The energetics of the electron transfer step in eqn. (6) is described in terms of the half-wave oxidation potential  $E_{1/2}^{\text{ox}}(\text{D}/\text{D}^{\ddagger})$  of the donor, the half-wave reduction potential  $E_{1/2}^{\text{red}}(\text{A}^-/\text{A})$  of the acceptor, the electronic excitation energy  $E_{0,0}^*$  of the excited molecule and the coulombic attraction

term  $C$  which refers to the energy change associated with the charge separation in a solvent of static dielectric constant  $\epsilon$ .  $C$  (eV) =  $-e^2/\epsilon R 4\pi\epsilon_0$  where  $e$  is the electronic charge,  $R$  is the centre-to-centre point-charge separation and  $\epsilon_0$  is the permittivity constant. In the derivation of eqn. (6), it was implicitly assumed that entropy changes accompanying the formation of the radical ion pair from the reactants are negligible and that the geometry of the excited state does not differ from the ground state. In practice entropic changes are always neglected when calculating overall energy changes.

The electrochemical potentials of NEC and molecule I in the ground electronic states together with their singlet and triplet excitation energies are presented in Table 5. These data allow  $\Delta G_{ET}$  to be calculated from eqn. (6), considering acetonitrile as a solvent ( $\epsilon = 37$ ) and two separation distances of the radical ions which correspond to the limiting interchromophore distances in the bichromophoric molecule II. Going from  $R = 3.75 \text{ \AA}$  to  $R = 8.6 \text{ \AA}$ , the coulombic term changes from  $-0.10 \text{ eV}$  to  $-0.05 \text{ eV}$  respectively. In fact when the solvent has a large dielectric constant (acetonitrile) the coulombic energy term is often neglected. The values of  $\Delta G_{ET} < 0$  presented in Table 6 clearly show that electron transfer from the carbazolyl chromophore to the 2,7-dinitrofluorene chromophore in II is exergonic and thus energetically probable [35] when one of the chromophores is in the excited electronic state. Furthermore, the conformational effect that the chromophores in the bichromophoric molecule have on the coulombic term is rather small and does not significantly change the  $\Delta G_{ET}$  values. Rehm and Weller [31] have determined that for  $\Delta G_{ET} < -10 \text{ kcal mol}^{-1}$  ( $-0.434 \text{ eV}$ ) the magnitude of the fluorescence quenching rate constant is diffusion limited ( $k_q \approx 2 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ ) for many organic reactants and remains constant as  $\Delta G_{ET}$  becomes more negative. For these systems (including NEC-molecule I)  $k_q$  can be calculated from the empirically derived expression

$$k_q = \frac{2.0 \times 10^{10}}{1 + 0.25\{\exp(\Delta G_{S,T}^*/RT) + \exp(\Delta G_{ET}/RT)\}} \text{ M}^{-1} \text{ s}^{-1} \quad (7)$$

where  $\Delta G_{S,T}^*$  is the activation free enthalpy of the reaction when one of the molecules is in the excited singlet or in the excited triplet state.

The following empirical relations between  $\Delta G_{S,T}^*$  and  $\Delta G_{ET}$  [31] and also between  $\Delta G_T^*$  and  $\Delta G_{ET}$  [36] have been proposed:

$$\Delta G_{S,T}^* = \frac{\Delta G_{ET}}{2} + \left[ \left( \frac{\Delta G_{ET}}{2} \right)^2 + \{\Delta G_{S,T}^*(0)\}^2 \right]^{1/2} \quad (7a)$$

in which  $\Delta G_{S,T}^*(0) = 0.104 \text{ eV}$  at  $\Delta G_{ET} = 0$ ;

$$\Delta G_T^* = \frac{\Delta G_{ET} + \alpha}{2} + \left\{ \left( \frac{\Delta G_{ET} + \alpha}{2} \right)^2 + \beta^2 \right\}^{1/2} \quad (7b)$$

in which  $\alpha = 0.104 \text{ eV}$  and  $\beta = 0.156 \text{ eV}$ .

TABLE 5

Ionization potential IP, electron affinity EA, half-wave polarographic oxidation and reduction potentials and first singlet and triplet energy levels for NEC (D) and for molecule I (A)

Compound	IP (eV)	EA (eV)	$E_{1/2}^{ox}(D/D^{\ddagger})$ (V)	$E_{1/2}^{red}(A^{\ddagger}/A)$ (V)	$E_S(D)$ (eV) ( $\pm 0.01$ )	$E_T(D)$ (eV) ( $\pm 0.01$ )	$E_S(A)$ (eV) ( $\pm 0.01$ )	$E_T(A)$ (eV) ( $\pm 0.01$ )
NEC	7.41 <sup>a</sup>	—	1.12 <sup>b</sup>	—	3.57 <sup>c,d</sup>	3.02 <sup>c,d</sup>	—	—
I	—	1.27 <sup>e</sup>	—	-1.02	—	—	3.42 <sup>c,d</sup>	2.46 <sup>c</sup> 2.48 <sup>d</sup>

<sup>a</sup> Value taken from ref. 32.

<sup>b</sup> Value taken from ref. 33.

<sup>c</sup> In acetonitrile at 77 K.

<sup>d</sup> In EPA at 77 K.

<sup>e</sup> EA in the gas phase calculated from EA = 0.81  $E_{1/2}$  + 2.10 (eV), where  $E_{1/2}$  is the half-wave reduction potential vs. the aqueous Ag/AgCl, saturated KCl reference electrode (see ref. 34).

TABLE 6

Free energies  $\Delta G_{ET}$  of the electron transfer process and calculated rate constants  $k_q$  of quenching of the excited singlet and triplet states in the NEC-molecule I system

Ground and excited electronic states of		$\Delta G_{ET}$ (eV)	$\Delta G_S^*$ (eV)	$\Delta G_T^*$ (eV)	$k_q$ ( $M^{-1} s^{-1}$ ) (296 K)
NEC (D)	Molecule I (A)	$R = 3.75 \text{ \AA}$	$R = 8.6 \text{ \AA}$		
D	A	+2.04	+2.09	—	—
$^1D^*$	A	-1.53	-1.48	—	$1.50 \times 10^{10}$
D	$^1A^*$	-1.38	-1.33	—	$1.49 \times 10^{10}$
$^3D^*$	A	-0.98	-0.93	$28.48 \times 10^{-3}$	$1.13 \times 10^{10}$
D	$^3A^*$	-0.42	-0.37	$72.00 \times 10^{-3}$	$3.84 \times 10^9$

The calculated values of  $k_q$  with  $\Delta G_{ET}$  at  $R = 8.6 \text{ \AA}$  are presented in Table 6.

These values characterize the intermolecular electron transfer quenching process in the NEC–molecule I system. The singlet or triplet electron transfer rate constants are of the order of  $10^{10} \text{ M}^{-1} \text{ s}^{-1}$  and are about equivalent to the diffusion rate constant in acetonitrile ( $2.8 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ ) [37]. However, the  $k_q$  values presented in Table 6 cannot directly characterize the interchromophoric electron transfer quenching process in the bichromophoric molecule II, because of the fixed distance between the interacting chromophores. Nevertheless, these theoretical values should be the lower limit of  $k_q$  for the bichromophoric molecule II in acetonitrile and EPA at room temperature and at 77 K if the conformation of the chromophores in II allows for good orbital overlap.

The electron-donor properties of the carbazolyl chromophore (for NEC, IP = 7.41 eV) and the electron-acceptor properties of the 2,7-dinitrofluorene chromophore (for I, EA = 1.27 eV) (Table 5) together with the calculated  $\Delta G_{ET} < 0$  for intramolecular electron transfer in the bichromophoric molecule, allows it to be concluded that the intramolecular charge transfer interactions in the excited electronic states of the bichromophoric molecule are energetically probable. However, such electron transfers will obviously be in competition with all other photoprocesses and/or with the spatial conformation changes of the donor and the acceptor in the bichromophore.

### 3.3.3. How energy transfer and electron transfer compete with the intramolecular photoprocesses

The rate constants of the intramolecular photoprocesses in the carbazole molecule studied in EPA at room temperature and at 77 K [21] together with the results for the energy and electron transfers summarized in Tables 5 and 6 allow us to draw conclusions about the quantitative aspect of all the intramolecular photoprocesses in the bichromophoric compound II presented in Scheme 1.

The energy transfer from the singlet excited carbazolyl chromophore to the 2,7-dinitrofluorene chromophore in the bichromophoric system (process 6, Scheme 1) at room temperature ( $k_{FT}^{296\text{K}} = 8.7 \times 10^{10} \text{ s}^{-1}$ ) and at 77 K ( $k_{FT}^{77\text{K}} = 1.3 \times 10^{11} \text{ s}^{-1}$ ) appeared to be much more probable than both the fluorescence of the carbazolyl chromophore ( $k_F(298\text{K}) = 2.7 \times 10^7 \text{ s}^{-1}$ ;  $k_F(77\text{K}) = 3 \times 10^7 \text{ s}^{-1}$ ) and the intersystem crossing process (process 4, Scheme 1) in the donor chromophore ( $k_{D_{isc}}(77\text{K}) = 3.7 \times 10^7 \text{ s}^{-1}$ ). This is probably the main reason why the fluorescence and phosphorescence of the carbazolyl chromophore are not observed. This also explains why processes 3b and 5 may not be competitive at all since very few  $^3D^*-A$  states are formed in the bichromophore II.

Moreover, the  $S_1^D \rightarrow S_1^A$  energy transfer process in the bichromophoric molecule also appeared to be more probable than the electron transfer quenching of the singlet excited carbazolyl chromophore by the

2,7-dinitrofluorene chromophore (process 3a, Scheme 1). However, according to  $\Delta G_{ET} < 0$ , the electron transfer quenching rate constant in the bichromophoric molecule II can be estimated as  $k_q \geq 10^{10} \text{ s}^{-1}$  for the high energy sandwich conformation of the chromophores. Nevertheless, such a high energy conformer of II can easily change to the low energy conformer of II where a very weak overlap exists between the chromophores [17]. In this case  $k_q$  would be lowered significantly.

In Scheme 1 the  $D-^1A^*$  state of the bichromophoric molecule is formed by the direct excitation of the 2,7-dinitrofluorene chromophore or by the interchromophore energy transfer process. This state of short lifetime is then rapidly transformed into the triplet  $D-^3A^*$  state by intersystem crossing (with the  $k_A^{isc} \geq 10^{10} \text{ s}^{-1}$ ). The deactivation of this triplet acceptor state gives rise to phosphorescence and to a radiationless pathway (see Scheme 1). Processes 2a and 2b are not efficient at all. Process 2a is probably not competitive with the intersystem crossing probability and process 2b even if it is much faster compared with  $0.5 \text{ s}^{-1}$  for the triplet decay has not been observed spectroscopically at low temperatures. This probably indicates that a particular conformational arrangement of the two chromophores is necessary for electron transfer to take place.

#### 4. Conclusions

In EPA at room temperature and at 77 K (as in 3-methylpentane and acetonitrile) no ground state charge transfer interaction appears to take place between the carbazolyl and the 2,7-dinitrofluorene (electron donor-acceptor) groups in the bichromophoric compound II. This is evidenced by comparing the absorption spectrum of II with the sum of the absorption spectra of the monochromophoric model compounds, NEC and molecule I.

Singlet excitation of the carbazolyl chromophore or the 2,7-dinitrofluorene chromophore do not give rise to the appearance of a new "intramolecular exciplex" or complex emission in the bichromophoric molecule II. Nevertheless, fluorescence and phosphorescence emissions of the carbazolyl chromophore are completely quenched in the bichromophore II and only the phosphorescence emission of the 2,7-dinitrofluorene chromophore in II is observed. The strong quenching effect of the excited singlet electronic state of the carbazolyl chromophore has been interpreted using the energy and electron transfer mechanisms. The  $S_1^D \rightarrow S_1^A$  energy transfer quenching mechanism involves the Förster long-range dipole-dipole interactions with a critical transfer distance  $R_0 = 28.6 \text{ \AA}$  at 296 K and  $30.4 \text{ \AA}$  at 77 K and with the rate constants  $k_{FT} = 8.7 \times 10^{10} \text{ s}^{-1}$  at 296 K and  $1.3 \times 10^{11} \text{ s}^{-1}$  at 77 K. This highly efficient photoprocess might compete with electron transfer and other intramolecular photoprocesses in the bichromophore II.

The high thermodynamic probability of the electron transfer quenching process in the bichromophore II has been analyzed by the theory of

Rehm and Weller in the limit  $\Delta G_{ET} < 0$ . We have shown that the process would be at least as fast as the diffusion-controlled reaction if the conformation of both chromophores were to allow for good orbital overlap. However, this photoprocess is strongly dependent on the steric conformation just in the same way as the Dexter type of energy transfer. The low energy conformation of the chromophores in II is such that very weak overlap between the orbitals of the chromophores exists at a distance of 8.6 Å.

In contrast, intramolecular energy transfer from the excited singlet or triplet states of the 2,7-dinitrofluorene chromophore to the carbazolyl chromophore is avoided (endothermic process). In such a situation, electron transfer interactions between the chromophores might also be competitive in the quenching of the excited singlet and triplet states of the 2,7-dinitrofluorene chromophore in II. However, since the phosphorescence lifetime and quantum yield of 2,7-dinitrofluorene remain the same in the bichromophore and in the polymer, this shows the low probability of the electron transfer process in the bichromophore and in the polymer at least at 77 K.

From the results discussed above, it appears that long-range singlet-singlet energy transfer (Förster type) from the carbazole moiety to the 2,7-dinitrofluorene chromophore is the dominant path in these systems. It is also apparent from the above results that conformational effects may play a major role in determining the probability of the electron transfer process. Since little is known about the effects that the mutual orientation of the donor and the acceptor have on electronic coupling it would be worthwhile concentrating on these effects in future work.

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