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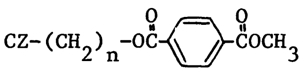
INTRAMOLECULAR EXCIPLEX FORMATION IN



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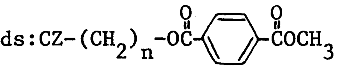
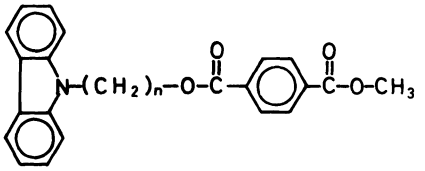
Compounds:



which show intramolecular exciplex emission have been synthesized, where CZ is the carbazole group and n = 1, 2,3,4, and 5. The absorption spectra and emission spectra of these compounds were studied; both normal fluorescence and intramolecular exciplex emission were strongly affected by methylene chain length. Very rapid exciplex formation (less than a few nsec) is indicated by the measurement of emission lifetime.

Recently extensive studies on intermolecular exciplexes formed between various organic electron donors and electron acceptors have been carried out,[1-3] but only a few have been reported on the intramolecular exciplexes.[4-7] In an early paper,[8] it was shown that the fluorescence of singlet excited N-ethylcarbazole is quenched by dimethylterephthalate (an electron acceptor) and a new exciplex emission band is observed in nonpolar solvents. In the present investigation, new compounds in which carbazole chromophore and terephthalic acid methylester are linked by methylene chains as shown in Fig. 1 were synthesized and the behavior of intramolecular exciplex emission has been investigated. Hereafter these compounds are denoted as I,II,III,IV,and V, indicating the number of methylene units.

Compounds: I,II, and III were prepared from corresponding N-hydroxyalkylcarbazoles by the reaction with terephthalic acid monomethylester chloride and purified by repeated recrystallization from acetone (for I,II) or cyclohexane (for III): m.p. 163-165°C(I), 176.5-178°C (II), 103-105°C (III). IV and V were obtained by the esterification of corresponding N-bromoalkylcarbazoles with terephthalic acid monomethylester silver salts and were recrystallized from n-hexane



I,	II,	III,	IV,	V,
n = 1,	2,	3,	4,	5,

Fig. 1.

several times: m.p. 67-70°C (IV), 79-80°C (V). Structures of these compounds were confirmed by 100 MHz n.m.r. spectroscopy, mass spectroscopy and elemental analysis.

The absorption spectra of these compounds in tetrahydrofuran solvent at the concentration of 10^{-4} mole/l are shown in Fig. 2. The absorption spectra of II- V are essentially the sum of the absorption spectrum of N-hydroxyalkylcarbazole and dimethylterephthalate, indicating that there is no appreciable ground state interaction between these two groups. In contrast to these compounds, the absorption spectrum of I is characterized by a considerable blue shift and spectral deformation, indicating that the electronic state of carbazole chromophore is slightly different from that of N-hydroxyalkylcarbazoles.

The fluorescence spectra of I-V and N-ethylcarbazole in 2-methyl THF solvent at the concentration of 10^{-4} mole/l are shown in Fig. 3. The fluorescence of carbazole is strongly quenched and a broad emission band appears at about 7000 cm^{-1} shifted to longer wavelengths than the normal fluorescence. Of course the equimolar solution of ethylcarbazole and dimethylterephthalate at this concentration neither quenches the normal fluorescence, nor gives emission bands other than that of N-ethylcarbazole. The excitation spectra of the broad emission band agrees well with the absorption spectrum of each sample, which is almost the same as that of corresponding N-hydroxyalkylcarbazole. Wavelength of this broad emission band maximum, is strongly affected by solvent polarity, i.e., it shifts to the longer wavelength with increasing solvent polarity. This behavior is quite similar to that of N-ethylcarbazole-dimethylterephthalate system. It is clear from the above results that the broad emission band in longer wavelength region is due to intramolecular exciplex formed between the pair of groups in the same molecule.

Decay times of the normal fluorescence and the broad emission band were measured at 25°C in 2-methyl THF solvent, using a single photon counting method. Risetime of the broad emission is instantaneous, following the exciting light pulse and decay profile of the broad emission bands is represented by a single exponential. Decay of the normal fluorescence of carbazole chromophore for all samples is very rapid, following the decay of exciting light pulse (half width of the light pulse $\sim$ 2 nsec). Some of the above results are summarized in Table 1: Maximum wavelength of exciplex emission (λ_e^{max}), quantum yield of the normal fluorescence of carbazole (Φ_m), apparent quantum yield of the exciplex emission (Φ_e) and lifetime of the exciplex emission (τ_e) are tabulated. Total quantum yield of normal fluorescence plus exciplex emission are considerably suppressed compared with the fluorescence quantum yield of ethylcarbazole ($\Phi \sim 0.47$). Both the degree of normal fluorescence quenching and the intensity of exciplex emission are strongly affected by the length of methylene chain. Normal fluorescence quenching decreases with the increase of methylene chain since the encounter frequency of excited carbazole moiety with the acceptor decreases with the increase of methylene chain. The largest Φ_e value and the longer τ_e for III indicate that trimethylene chain is especially effective for intramolecular exciplex. This may be due to the favorable steric situation of trimethylene chain upon exciplex configuration and relatively high

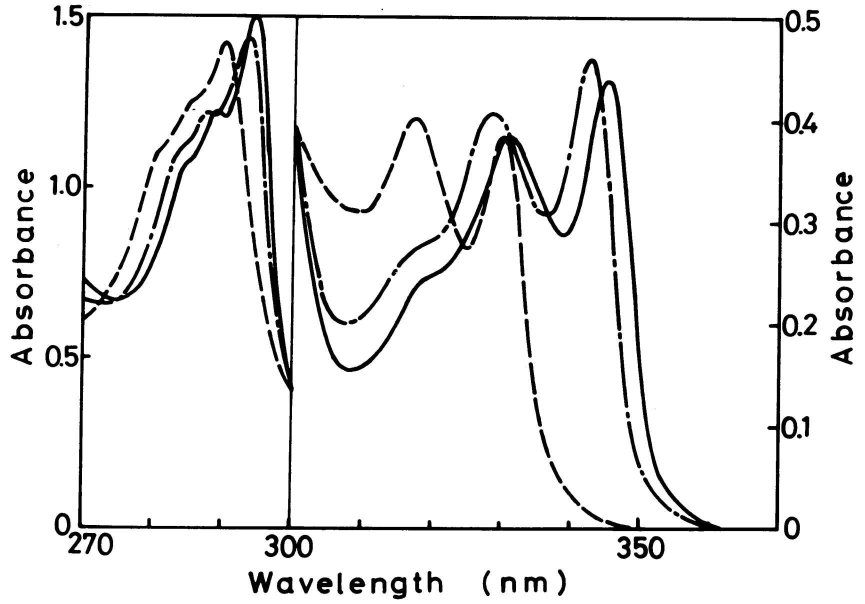


Fig. 2. Absorption spectra of the compounds, 1-V. Concentration: 1.0x10^{-4} mole/l; Solvent: THF.

— — — — — : I; —•—•— : II; ———— : III-V.

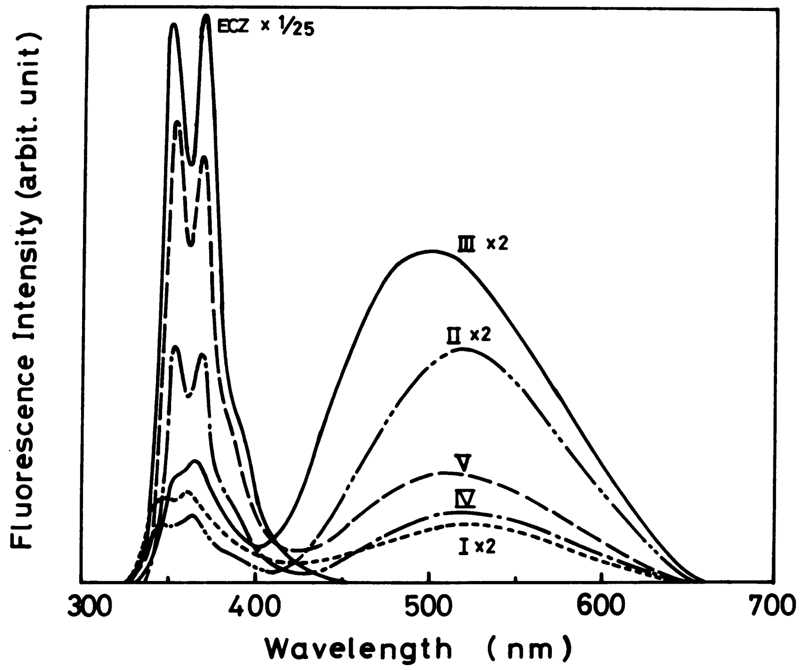


Fig. 3. Emission spectra of the compounds, I-V and N-ethylcarbazole at room temperature. Concentration: 1.0x10^{-4} mole/l; Solvent: 2-methyl THF.

Table 1.

	$\lambda_e^{max.}$ (nm)	$\Phi_m \times 10^3$	$\Phi_e \times 10^3$	τ_e (nsec)
I	510	≤ 1.5	7.4	9.8
II	510	≤ 1.0	26.3	21.3
III	480	2.1	51.5	34.6
IV	515	6.0	16.1	21.0
V	490	10.2	27.5	37.4

encounter frequency. In I,II and IV, the strain in methylene chain in the exciplex state may be larger than that for III, and this makes the exciplex unstable, so τ_e's are shorter and accordingly, Φ_e's are smaller than that for III. The encounter frequency in V is lower than that in IV, but conformational strain may be rather small due to the longer methylene chain. Hence the exciplex is more stable and τ_e or Φ_e becomes larger than that for IV. Effect of molecular structure and Brownian motion upon the normal fluorescence quenching and the exciplex formation are being studied in detail and will be published in the near future.

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