

# Intramolecular Excited-State Charge-Transfer Interactions and the Role of Ground-State Conformations

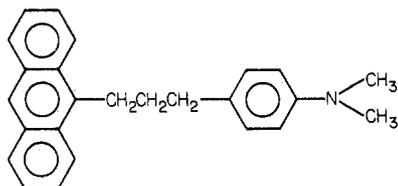
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The dynamics of formation of the intramolecular exciplex, anthracene-(CH<sub>2</sub>)<sub>3</sub>-*N,N*-dimethylaniline, has been investigated by using a picosecond laser-streak camera system. Measurement of the fluorescences of both the excited-state acceptor decay and exciplex rise demonstrate that there is no intermediate nonfluorescent state prior to exciplex formation and that the end-to-end relaxation is exponential. Furthermore, a dependence of exciplex rise time upon the fluorescence wavelength is found and interpreted as evidence for two distinct ground-state conformers, one being dominant.

## Introduction

An electronically excited molecule can relax its energy through charge-transfer (CT) interactions with surrounding ground-state molecules, leading to exciplex formation in nonpolar solvents and the formation of ions in polar solvents. The diverse physical and chemical nature of these processes have been extensively studied since the pioneering work of Leonhardt and Weller.<sup>1</sup> Of particular interest is the role of geometric effects, i.e., the relative orientations of the donor and acceptor molecules on the dynamics of exciplex formation. From our previous studies<sup>2</sup> on the intermolecular exciplex formation between anthracene and *N,N*-diethylaniline (DEA) molecules it was established that upon excitation of anthracene an electron can jump from DEA to the excited anthracene over a reaction distance of 8 Å within 10 ps. By connecting the anthracene and DEA molecules with three methylene groups (I), the relative orientations of the molecules are



I

restricted while still maintaining their close proximity, maximum separation between them being less than 4 Å.

Upon excitation, this model molecule should form an intramolecular exciplex as rapidly as the free anthracene and DEA system, if there are no significant orientational requirements for CT interaction. On the other hand, if the time course for exciplex formation is different for the two cases, then molecular motions to achieve a favorable geometry must be involved and can be directly followed in the formation of the intramolecular exciplex. This principle has been applied in previous studies<sup>3,4</sup> by monitoring the exciplex adsorption at 694 nm. However, the results obtained in these studies were in conflict possibly due to nonlinear intensity-dependent absorption which would produce species absorbing in the exciplex region. This could be responsible for the rapid rise time observed in one of the studies.<sup>4</sup>

To avoid these complications lower laser intensities were used in the present study. Furthermore, a complementary technique, namely picosecond time-resolved fluorescence

of both the excited anthracene decay and exciplex formation at several different wavelengths, is employed to obtain the dynamics of the charge-transfer process. The results confirm the finding of one of the previous studies.<sup>3</sup> In addition, we have observed an unexpected dependence of the rate of exciplex formation on the fluorescence wavelength monitored. This observation is interpreted in terms of the effect of different ground-state conformations upon the rate of intramolecular exciplex formation.

## Experimental Section

A TEM<sub>00</sub>, 4–8 ps, third-harmonic pulse (351 nm) from a passively mode-locked Nd<sup>3+</sup>-phosphate glass laser was used to excite the anthracene moiety. The fluorescence and the excitation pulse width were monitored with an Imacon streak camera coupled to a PAR optical multi-channel analyzer. Streak speed is calibrated with an etalon. Linearity of the intensity response is checked in every experiment and the streak camera-OMA response function is corrected in each shot.

The synthesis of 9-anthracene-(CH<sub>2</sub>)<sub>3</sub>-*N,N*-dimethylaniline has been described before.<sup>3</sup> The crude compound was first purified by recrystallization from ethanol-water and petroleum ether. A portion was then further purified by thin-layer and spinning-band chromatography and checked by high-performance LC and NMR. Fluorescence spectra show no difference between the compound purified by chromatography and that purified by recrystallization only. Excitation spectra taken at several different wavelengths (410, 480, 560 nm) are in excellent agreement. Experiments were performed with the recrystallized compound and the chromatographically purified compound and yielded identical results. Isopentane was obtained from Aldrich (99+%). It was purified by passing through a neutral alumina column before use. The sample solution was deoxygenated by repetitive freeze-pump-thaw cycles. All experiments were done at 20 °C.

## Results and Discussion

A 351-nm picosecond laser pulse was used to excite the anthracene moiety in the model compound. The decay of anthracene fluorescence in isopentane was monitored at 410 nm and the result is shown in Figure 1. It can be fitted with an exponential curve with decay constant of  $1.4 \pm 0.1$  ns. The observed single exponential decay is quite different from the two exponential decay behavior which is characteristic of the reverse dissociation generally observed in other exciplex and excimer systems. This reflects the unusual stability of the anthracene-(CH<sub>2</sub>)<sub>3</sub>-

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emissions do not significantly overlap in wavelength.

At present, it is not clear what structures actually correspond to the ground-state conformers in the model compound. Nor do we understand the exact nature of the two different rotational motions. We are currently investigating the viscosity and temperature dependence of these dynamic processes in order to gain a better understanding of these issues. Preliminary results show the same behavior in hexane solution, where the formation rate of exciplex at 570 nm is slower than at 520 nm, being 2.6 and 1.9 ns, respectively.

### Note

During the course of writing this paper, two relevant articles appeared in the literature. Van der Auweraer et al.<sup>14</sup> studied the intramolecular exciplex formation of 3-phenyl-1-(dimethylamino)propane and reached the similar conclusion that there are two different ground-state conformers leading to the exciplex formation with different rates. However, only one exciplex emission was detected in their system. Another paper by Migita et al.<sup>15</sup> reported a time-resolved fluorescence study on the same intramolecular exciplex system investigated here. They determined the exciplex formation time in hexane to be 2.6 ns in the wavelength region 540 nm and above, which is exactly what we find. However, they did not monitor the fluorescence rise at shorter wavelengths where we detected the faster exciplex formation.

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