tions favorable to these emission signals are more readily achieved by prolonged heating of the film. Presumably rotation and translation of chain segments at elevated temperatures provide a mechanism for achieving more thermodynamically stable chain configurations. Similar effects have been observed for singlet excimer emission from polystyrene and other vinyl aromatic polymers.[1]

A concluding comment should be added here concerning the delayed fluorescence lifetime observed for PFCZ in frozen MTHF. It is clearly less than one-half of the phosphorescence lifetime; it is also clear that it originates in triplet–triplet annihilation. Of necessity, therefore, the pool of triplet-state chromophores responsible for delayed fluorescence and that responsible for the long-time component of the phosphorescence are distinct but perhaps overlap to some extent. Cozzens and Fox[18] have discussed this effect concluding that triplet–triplet annihilation must occur by an intramolecular migration of triplet excitons. This, in effect, means that there is a nonhomogeneous distribution of triplet chromophores among chain molecules and that only limited intermolecular triplet migration can occur in these rigid solutions.

## Conclusions

The subject polymer PFCZ and its monomeric analogue MFCZ display photophysical properties which are significantly different from poly(*N*-vinylcarbazole). The strong blue shift of the fluorescence of PFCZ relative to PVCA has been related to the nature of the substituent groups bonded to the carbazole nitrogen atom. The very weak excimer fluorescence in PFCZ has likewise been related to the nature of these substituents and to a less constrained steric environment. Phosphorescence and delayed fluorescence spectra and kinetics in solid films of PFCZ suggest that, although excimer-forming sites exist in the polymer film, they are less populous than in PVCA. Furthermore, the relative populations of the two types of sites present are sensitive to the thermal history of the samples. The mechanism of delayed fluorescence production both in solid films and in rigid solutions of PFCZ is triplet–triplet annihilation.

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**Registry No.** II, 56995-05-2; ethyl chloroformate, 541-41-3; carbazole, 86-74-8.

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# Intersystem Crossing and Triplet-State Properties of Dinaphthyl Compounds

**James F. Pratte† and Stephen E. Webber***

*Department of Chemistry and Center for Polymer Research, University of Texas at Austin, Austin, Texas 78712*

**F. C. De Schryver***

*Department of Chemistry, Universiteit Leuven, Celestijnenlaan 200 F, B-3030 Heverlee, Belgium.* *Received December 13, 1983*

ABSTRACT: Triplet–triplet absorption spectra have been measured for diastereoisomers of bis[1-(1- and 2-naphthyl)ethyl] ethers and 1,3-di-$\beta,\beta'$-naphthylpropane. There is no evidence for triplet excimer formation in any of these compounds. In general there is a decrease in the quantum yield of intersystem crossing for those stereoisomers that exhibit a stronger excimer fluorescence (i.e., $\Phi_{isc}^{meso} < \Phi_{isc}^{racemic}$) but the differences in $\Phi_{isc}$ are as large between 1- and 2-naphthyl substitution as between meso and racemic stereoisomers. In the case of *meso*-bis[1-(2-naphthyl)ethyl] ether an anomalously short triplet lifetime was observed.

## Introduction

In recent years dichromophoric compounds have been widely used as models for polymeric pairwise sequences and have been very successful in elucidating the photophysical properties of the singlet state of polymers. In particular for diastereoisomers of dichromophoric compounds it has been demonstrated that there is a very strong dependence of the monomer-to-excimer fluorescence ratio and the nature of the excimer state on the stereoisomerism (i.e., in most cases the meso stereoisomer has a much stronger excimer fluorescence than a racemic stereoisomer).[1,2] These differences can be understood in terms of the population distribution of various conformers of these model compounds.

In a number of polymer systems it has been observed that the triplet yield ($\Phi_{isc}$) is greatly diminished relative

†Present address: Du Pont, Wilmington, DE.

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Table I
Singlet- and Triplet-State Photophysical Constants for Naphthyl Compounds

| compd | $\Phi_{fl}$[a] | $\Phi_{fl}^D/\Phi_{fl}^M$[b] | $\Phi_{isc}$[a] | $k_T \times 10^{-4}$, $s^{-1}$ |
|---|---|---|---|---|
| naphthalene (cyclohexane) | 0.23[c] | | 0.75[d] | 3.4 ± 0.12 |
| 1-methylnaphthalene (cyclohexane) | 0.25[c] | | 0.58[d] | |
| 2-methylnaphthalene (cyclohexane) | 0.32[c] | | 0.56[d] | |
| 1,3-di-β,β'-dinaphthylpropane | 0.16 ± 0.02 | 7.7 | 0.42 ± 0.04 | 6.2 ± 0.20 |
| *meso*-D2NEE | 0.044 ± 0.004[f] | *e*, *g* | 0.28 ± 0.03 | 182.5 ± 0.09 |
| *rac*-D2NEE | 0.084 ± 0.008[f] | 0.19[g] | 0.49 ± 0.05 | 8.9 ± 0.17 |
| *meso*-D1NEE | 0.017 ± 0.002[g] | 4.7[e,g] | 0.12 ± 0.01 | 6.5 ± 0.04 |
| *rac*-D1NEE | 0.095 ± 0.01[f,g] | 2.2[g] | 0.31 ± 0.03 | 6.1 ± 0.16 |

[a] All values for isooctane at room temperature unless otherwise stated. This work unless otherwise stated. [b] Ratio of excimer-to-monomer fluorescence quantum yields, obtained by fitting total spectrum to monomer and excimer components. [c] From: Berlman, I. B. "Handbook of Fluorescent Spectra of Aromatic Molecules", 2nd ed.; Academic Press; New York, 1971. [d] Amand, B.; Bensasson, R. *Chem. Phys. Lett.* **1975**, *34*, 44. [e] Because of the large overlap of monomer and excimer emissions and the weakness of the monomer emission it is difficult to determine this ratio accurately, but it is certainly ≥5. [f] DeSchryver, F. C., unpublished results. [g] From ref 1b.

to a simple monomeric model compound (e.g., compare 2-methylnaphthalene with poly(2-vinylnaphthalene)) although other triplet properties (i.e., lifetime and T–T absorption) have been found to be essentially the same as the monomeric model.[3] There are at least two reasonable origins for this effect: (1) intracoil singlet–singlet annihilation, and (2) diminished intersystem crossing from $^1M^*$ ("monomeric" excited state) and/or from $^1D^*$ (excimer excited state; note that there may be several types of excimer states depending on the degree of overlap of the two chromophores). The former is much more important for polymers than for small molecules because of the high local concentration of chromophores, but can be avoided by decreasing the intensity of the excitation source.[3a] It would be reasonable to expect dichromophoric model compounds to demonstrate the importance of the latter phenomena because of the overall similarity of their $^1M^*$ and $^1D^*$ states to those of the polymer. It is this aspect of dichromophoic photophysics that we report in this paper.

We may summarize our observations as follows: (1) The triplet yield of the dichromophoric naphthalene compounds is diminished relative to the appropriate monomeric model compounds, but this diminution is not related simply to the ease of formation of the excimer state. (2) The T–T absorption spectrum is very similar to the monomeric model compound and there is no spectroscopic evidence for a triplet excimer at room temperature. (3) The triplet lifetime in outgassed isooctane at room temperature is very similar for all compounds except racemic bis[1-(2-naphthyl)ethyl] ether (D2NEE), in which case $\tau_T$ is decreased by a factor of ca. 20 relative to the meso isomer. At present we do not have an explanation for this striking difference.

## Experimental Section

The synthesis and characterization of the racemic and meso D2NEE and bis[1-(1-naphthyl)ethyl] ether (D1NEE) has been described previously.[1b] The triplet quantum yield was measured by using the relative actinometry method of Amand and Bensasson.[4] Naphthalene was used as the standard with a $\Phi_{isc}$ value of 0.75.[4] Cyclohexane (spectrograde MCB) and isooctane (Gold Label, 99%, Aldrich) were used as received. The laser flash photolysis system at the Center for Fast Kinetics Research, University of Texas at Austin, that was used for the work described herein will be described in a future publication.[3] A Quantel YG 481 Nd:YAG Q-switch laser (λ = 266 nm, 11-ns pulse width, 70-mJ maximum energy) was used as the excitation source. The laser intensity was attenuated by neutral density filters for both spectra and $\Phi_{isc}$ measurements. The laser beam is focused on a slit image that was parallel to the monitoring beam which sampled the first millimeter of the cuvette. The monitoring beam is a 150-W xenon lamp that could be run in a continuous or pulsed mode. The lamp pulser was a PRA Model M-305 which produced an intense pulse that was flat (signal base line) over 20 μs. Monochromator bandwidths were 3 nm for the $\Phi_{isc}$ measurement and 6 nm for the transient absorption spectra. The transient absorption spectra were produced by assembling decay curves at 5-nm intervals. The quoted $\Phi_{isc}$ values were the averaged values from four different low laser intensities (e.g., range $3.8 \times 10^{14}$ –$2.9 \times 10^{15}$ photons/cm$^2$). The laser intensity for the transient absorption spectra was raised to $1.3 \times 10^{16}$ photons/cm$^2$ in order to obtain high-quality spectra. The rates of decay of the triplet state for the samples were obtained by fitting the data to a single exponential at low laser intensities. The decay curves were adequately fitted to a single exponential with no noticeable second-order component (i.e., there is no triplet–triplet annihilation). Data processing and storage were performed on a PDP11/70 computer. The optical density of a 1-cm path length of the solutions was 0.5 at the laser wavelength. Fluorescence quantum yields and decomposition of the fluorescence spectra into components were determined as reported previously.[5] Naphthalene in cyclohexane ($\Phi_{fl}$ = 0.23) was used as a standard.

## Results

**T–T Absorption.** In Figure 1 are the triplet–triplet (T–T) absorption spectra of the meso and racemic isomers of D2NEE and D1NEE in isooctane at room temperature. All the spectra are naphthalenic in appearance with both stereoisomers of the same compound having almost identical spectral features. The T–T absorption bands of the D1NEE isomers are red shifted relative to those of the D2NEE isomers by a few nanometers. Because of the similarity of the $\lambda_{max}$ values for the T–T absorption for these compounds to those reported for 1-methylnaphthalene and 2-methylnaphthalene,[4] the molar extinction coefficients of the T–T absorption for 1- and 2-methylnaphthalene were used in the estimation of $\Phi_{isc}$ for the isomers of D1NEE and D2NEE. The maximum of OD for each spectrum is proportional to $\Phi_{isc}$ in Table I.

**Quantum Yield and Lifetime Data.** Table I lists the values of $\Phi_{isc}$ for the isomers D1NEE and D2NEE as well as the rate of decay of the triplet state. The $\Phi_{isc}$ values are also listed for naphthalene, 1-methylnaphthalene, and 2-methylnaphthalene as reported by Amand and Bensasson.[4] As can be seen, the $\Phi_{isc}$ values for the various isomers of D2NEE and D1NEE are less than their monomeric model compound counterparts with the $\Phi_{isc}$ values for meso stereoisomers significantly reduced from those of the corresponding racemic stereoisomers. It will be noted that the $\Phi_{isc}$ values of the D2NEE isomers are greater than their analogous isomers for D1NEE. The rates of decay for the triplet state of the stereoisomers of D1NEE are almost identical while that of the meso isomer of D2NEE is almost 20 times that of the racemic isomer. The same unimolecular decay rate was observed if the *meso*-D2NEE was sensitized by the biphenyl triplet. For both excitation conditions the triplet concentration was sufficiently low that triplet–triplet annihilation can be neglected. While lifetime studies of triplet states in fluids are always plagued

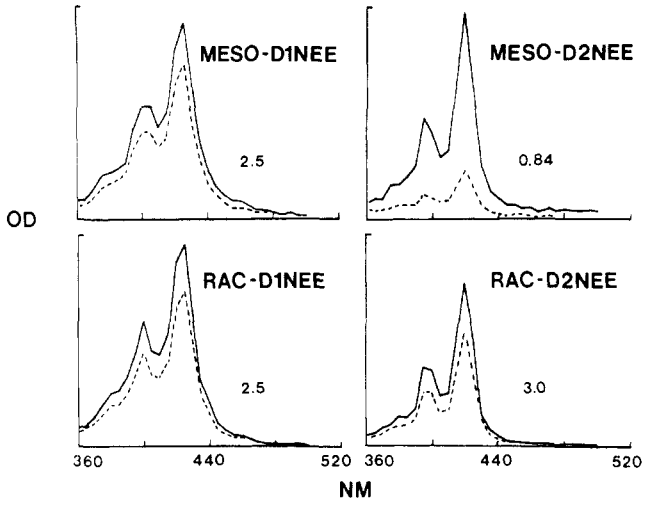


**Figure 1.** T–T absorption spectra at times indicated for isomers indicated of dinaphthyl ethers (OD in arbitrary units, path length = 1 cm). All spectra in isooctane at room temperature following 266-nm pulse (11-ns). The solid line is the spectrum <1 μs after the laser pulse and the dashed line is for the time indicated (in microseconds) after the first spectrum (the bandwidth of the monochromator was 6 nm).

by the presence of trace impurities,[6] we believe that a meaningful comparison of a homologous series of compounds is possible if one uses the same solvent purification procedures and outgassing procedures. Consequently we ascribe the difference in $k_T$ for *meso*-D2NEE from the remainder of the naphthyl compound to an intramolecular process. However, there does exist the possibility that some quenching impurity was present in *meso*-D2NEE that was not removed by the same chromatographic methods used for all materials studied herein.

## Discussion

Since the early proposal of face-to-face sandwich excimers and the Hirayama "$n = 3$" observation for dichromophoric alkanes[7] it has been found that the situation with respect to singlet and triplet excimer formation is more complex than originally envisioned. In particular there may exist a variety of partially overlapping excimer conformation with different fluorescence spectra, quantum yields, and lifetimes. The existence of triplet-state excimers has not been unequivocally established for a broad range of compounds but for naphthyl[8] and phenanthryl[9,10] observation of triplet excimers has been claimed.

For dichromophoric compounds certain general conclusions have emerged.

(1) The extent of singlet excimer formation depends not only on the stabilization of the excimer, which in turn depends on the strength of the transition dipole and the orientation of the pair of chromophores, but also on the configuration, conformational distribution, and the steric hindrance to the required intramolecular rotations. This is exemplified by the study of diastereoisomers by DeShryver et al.[1a,b,2] and Ito et al.[1c] Zachariasse et al.[9] have also demonstrated the effect of the substitution position of propyl chain attachment in the case of diphenanthryl propanes.

(2) A configuration that maximizes the stability of the singlet excimer does not necessarily stabilize the triplet excimer. A case in point is 1,3-di-9,9′-phenanthrylpropane, for which Zachariasse et al.[9] report a very small singlet excimer quantum yield, but a very significant triplet excimer yield (and a shortened triplet lifetime). There are also reports in the literature of very strong perturbation in the fluorescence and phosphorescence spectra of certain dinaphthylcyclophanes,[11] which almost certainly is the result of different types of naphthalene–naphthalene overlaps.

There are two general observations from the results reported herein:

(1) Despite a very large range of singlet excimer formation quantum efficiencies (as reflected by $\Phi_{fl}^d/\Phi_{fl}^m$ in Table I) there is no spectroscopic evidence for the existence of a triplet excimer for any of the dinaphthyl compounds in Table I (see Figure 1).

(2) In general $\Phi_{isc}$ is diminished for a given substitutional isomer for the meso stereoisomer. We note that this is always the stereoisomer with the largest $\Phi_{fl}^D/\Phi_{fl}^M$ ratio, but that there is certainly no simple relationship between $\Phi_{fl}^D/\Phi_{fl}^M$ and $\Phi_{isc}$ (compare *meso*-D2NEE and *rac*-D1NEE, which have almost the same value of $\Phi_{isc}$ but vastly different excimer/monomer ratios). We note that the value of $\Phi_{isc}$ for the dinaphthyl compounds in Table I is generally 2–3 times higher than for poly(2-vinylnaphthalene) even though the overall fluorescence quantum yield and excimer/monomer fluorescence ratio for the polymer are similar to those of the dinaphthyl compounds. It seems clear that more extensive chromophore–chromophore interactions enhance the internal conversion rate from the singlet manifold.[3]

One anomalous observation is the large decay rate from the triplet state of *meso*-D2NEE (see Table I). We have no firmly based explanation for this enhanced rate. We can only speculate that for the meso isomer with 2-substitution a pairwise conformation of the two naphthalenes is possible that enhances the radiationless $T_1 \rightarrow S_0$ rate without perturbing the T–T absorption spectrum.

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