

Excited State Electron and Energy Transfer of a Highly Fluorescent Heterocyclic Dye: a Laser Flash Photolysis Study of 2,5-Dimethyl-3,6-diphenylpyrrolo[3,4-*c*]pyrrole-1,4-dione

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The triplet and singlet state properties of the title compound are reported: nitroxyl free radicals and oxygen enhance the triplet yield significantly; electron transfer from the singlet excited state to methyl viologen in acetonitrile produced the corresponding free radicals which recombine with second-order kinetics.

2,5-Dimethyl-3,6-diphenylpyrrolo[3,4-*c*]pyrrole-1,4-dione (DMDPP) belongs to a new class of heterocyclics called the diketopyrrolopyrroles which are finding use in a variety of industrial applications, especially as pigments.¹ These systems have been explored for applications in non-linear optics² and a derivative of DMDPP has shown promise for optical data storage.³

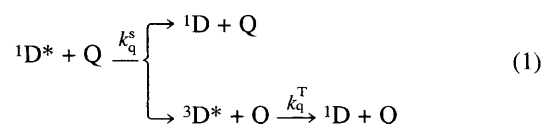
Some data on the optical absorption spectra of DMDPP in solution have been reported,^{4,5} but little information exists on the emission and the triplet state behaviour of this technologically important molecule. Here we report our results on the triplet state, studied using nanosecond laser flash photolysis.

DMDPP (Ciba-Geigy), TEMPO (2,2,6,6-tetramethylpiperidine *N*-oxyl, Fluka) and methyl viologen (Fluka) were used without further purification. For recording the transient spectra, the Ar-bubbled solutions were excited at 347 nm by a Ruby laser (JK Lasers, 20 ns pulse-width, average power 10–15 mJ/pulse). The transient absorption signals were detected using a photomultiplier tube (PMT) and the Tektronix DSA 602A acquisition system using a xenon lamp for probing. The data were transferred to a Macintosh computer for analysis. The solvents used were of spectroscopic grade (Fluka). The absorption spectra were recorded by a Cary-5 spectrometer and the corrected fluorescence spectra were recorded using a SPEX

fluorolog spectrometer. The fluorescence quantum yield was determined using Rhodamine B in ethanol as a standard.⁶

The longest wavelength absorption band of DMDPP is a $\pi\pi^*$, HOMO to LUMO transition as determined by semi-empirical calculations using INDO/1 parameters.⁷ The absorption and emission spectra of DMDPP in dioxane are shown in Fig. 1. The absorption spectrum of DMDPP is quite broad and featureless, but the emission spectrum shows good vibrational structure. The absorption and emission maxima in dioxane are at 476 and 526 nm, respectively. Since the molecule is known to be non-planar (from the crystal structure),⁸ poor Frank-Condon overlap between the ground and the first excited state is expected to result in a loss of vibrational structure. In ethanol and dioxane the fluorescence quantum yield (Φ_f) of DMDPP was determined to be 0.9 ± 0.05 and approaches unity upon removing oxygen from the solvents. The fluorescence lifetime (τ_f) in ethanol was measured to be 6.0 ns using time-correlated single photon counting technique.⁷ In ethanol the spectra are slightly blue-shifted by 5 nm and the absorption and emission maxima are at 470 and 522 nm, respectively.

The bimolecular quenching process leading to the quenching of triplet and singlet excited states is described by eqn. (1), where D is DMDPP and Q is either oxygen or TEMPO, k_q^s and k_q^T are the bimolecular quenching rate constants for the singlet and triplet excited states, respectively.



Both oxygen and TEMPO are found to quench the singlet excited state of DMDPP with nearly diffusion controlled rate constants. The experimental values of k_q^s in dioxane for oxygen and TEMPO are 5.8 and $6.9 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, respectively, determined by steady-state fluorescence quenching measurements. The triplet quenching rate constants k_q^T for oxygen and TEMPO are found to be 2.3×10^9 and $3 \times 10^6 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$,

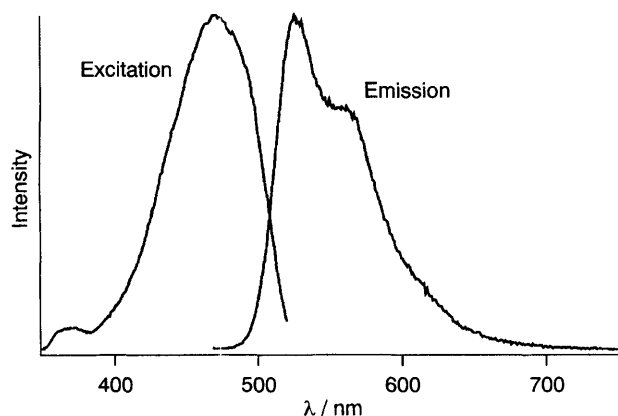
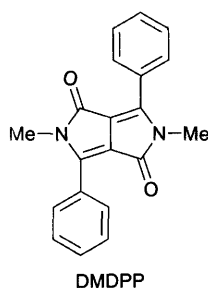


Fig. 1 Excitation and emission spectra of DMDPP in dioxane. For the emission, λ_{ex} was 450 nm and λ_{em} was 600 nm for the excitation spectrum.

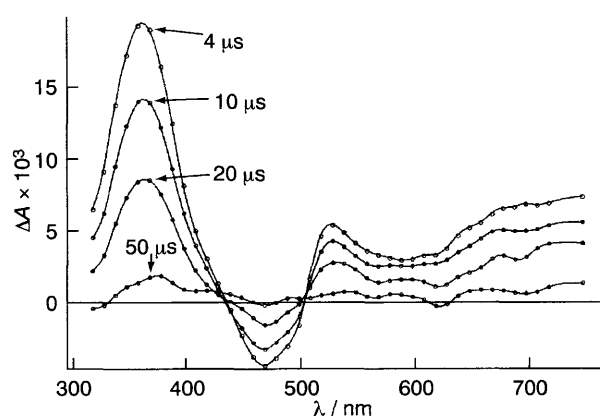


Fig. 2 Triplet-triplet absorption spectra of DMDPP in dioxane at different times after the laser pulse, in the presence of 20 mmol dm^{-3} of free radical TEMPO

respectively and are determined from the triplet decay measurements. The triplet quenching rate constant of TEMPO is slower by *ca.* 3 orders of magnitude, compared to oxygen. It is known that efficiencies for quenching of triplets by nitroxyl are known to decrease for low lying triplets.⁹ Further studies are required to understand this discrepancy.

The triplet yield of DMDPP was enhanced significantly in the presence of oxygen or a free radical like TEMPO. By measuring the increase in triplet absorbance in the presence of oxygen or TEMPO we determined δ/ϕ_0^T , using the procedure of Das *et al.*,⁹ where δ is the fraction of singlets giving rise to triplets upon bimolecular quenching and ϕ_0^T is the triplet quantum yield without quencher. Using an estimated value of 1% for triplet quantum yield, we find δ values of 1.0 and 0.7 for oxygen and TEMPO, respectively. The free radical TEMPO is slightly less efficient than oxygen in promoting intersystem crossing and the possible explanation is the contribution of internal conversion to the nonradiative deactivation of the singlet excited state.

We have taken advantage of high triplet enhancement and weak triplet quenching by TEMPO to record triplet-triplet absorption spectra. Fig. 2 shows the transient absorption spectrum of DMDPP in dioxane in the presence of 20 mmol dm⁻³ of TEMPO. The transient was assigned to the triplet state on the basis of triplet energy transfer experiments using the triplet of anthracene as donor. The triplet-triplet absorption spectrum shows a strong ground state bleaching signal with the maximum depletion occurring near the absorp-

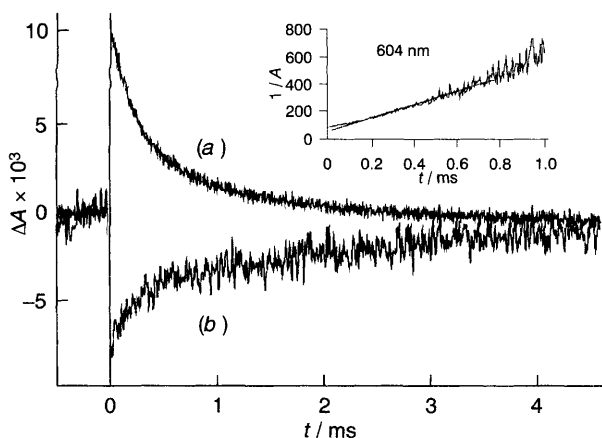


Fig. 3 The recombination kinetics of MV^{+•} at 604 nm (a) and the recovery of DMDPP ground state at 470 nm (b). The inset shows a fit to second-order kinetics for the 604 nm decay.

tion maximum at 470 nm. The longest triplet lifetime measured for DMDPP in degassed dioxane was 170 μ s under our conditions. The long triplet lifetime of DMDPP, a symmetric non-planar heterocyclic system, is similar to what is observed for aromatic hydrocarbons.¹⁰ The central position of the molecules has a 1,4-diphenylbutadiene segment, in a rigid *trans* configuration which prevents the torsional motion of the diene fragment and therefore may not contribute to the nonradiative deactivation of the excited states. The triplet energy was estimated to be between 30 and 35 kcal mol⁻¹ (1 cal = 4.184 J) using suitable triplet donors.

The singlet excited state of DMDPP is efficiently quenched by methyl viologen in acetonitrile resulting in the production of radicals as shown in eqn. (2).

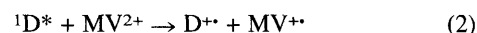


Fig. 3 shows the recovery of the ground state of DMDPP at 470 nm and the monocation of methyl viologen at 604 nm. The inset of Fig. 3 shows a fit for second-order kinetics for the 604 nm decay. The radical recombination rate constant was found to be 7×10^9 dm³ mol⁻¹ s⁻¹. The radical cation of DMDPP does not seem to absorb in the visible region. Steady-state irradiation experiments with methyl viologen in acetonitrile did not result in the production of MV^{+•} radical after prolonged irradiation ($\lambda > 400$ nm) which was well explained by the observations of the time-resolved experiments.

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