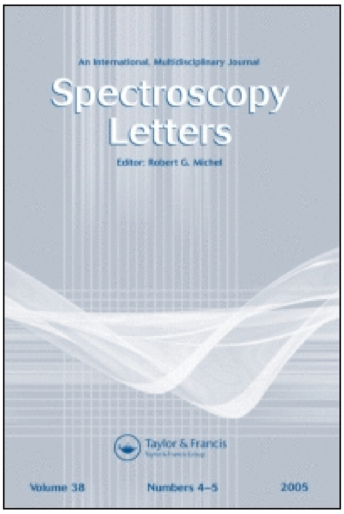

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Laser Induced Lowest Triplet State Properties of Dibenzothiophene in Solution

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Laser Induced Lowest Triplet State Properties of Dibenzothiophene in Solution

Key words:
Triplet state
P-Type delayed fluorescence
Quenching
Dibenzothiophene
T-T absorption spectrum

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Abstract

Laser induced triplet state lifetimes are measured in the presence of air and for oxygen, air, argon saturated, and vacuum degassed solution of

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**All correspondance should be addressed dibenzothiophene in solution at room temperature by triplet decay, including the prompt and p-type delayed fluorescence. The results are discussed and compared to those of molecules with the same symmetry.

1. Introduction

The dibenzothiophene molecule is slightly non-planar, being bent about the Z axis so that the angle between the two benzene rings is 178.7°. The deviation from planarity which may be due to the packing forces in the crystal is small and the free molecule is treated as having full C_{2v} symmetry,[1]. In the complex dibenzothiophene absorption spectrum in solution, the two systems at 326 nm and 287 nm almost certainly represent separate transitions, but each of the more complicated regions begining at about 268 nm and 245 nm may represent more than a single electronic transition. The dibenzothiophene is confined to assign the symmetry of the lowest-energy singlet electronic state to investigate the vibrational structure of this excited state from the absorption spectrum, and to study the ground state vibrational structure from fluorescence and phosphorescence spectra[2]. The longest wavelength member of the absorption spectrum of dibenzothiophene, prompt fluorescence in ethanol at room temperature is presented in figure 1. Two-photon fluorescence excitation spectra of dibenzothiophene crystal (77 K) and in solution have been investigated in the spectral region 260-335 nm. It has been found that the intensity of the first electronic band system arises not only from a purely electronic mechanism, but also from its interaction with a higher state through totally symmetric vibrations. In systems without inversion center, such as dibenzothiophene, the selection rule does not apply as there are states both one and two-photon active[3]. Polarized dye-laser two-photon excitation spectra are reported for dibenzothiophene and some bridged compounds are compared with the biphenyl two-photon spectrum[4]. The work reported here was

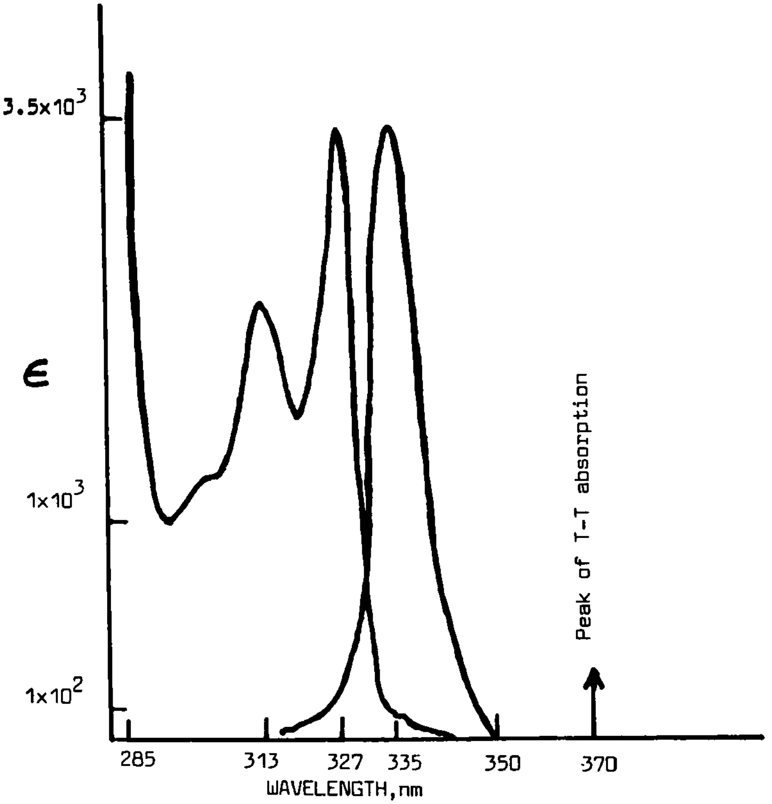

Fig. 1. The longest wavelength absorption band and prompt fluorescence spectra of dibenzothiophene, in ethanol at room temperature.

undertaken with the aim of determining the values of photophysical parameters which are of significance to the photochemistry of the excited singlet and triplet states.

2.Experimental

The dibenzothophene was "Ega chemie" reagent grade and used as received, all other chemicals used were also reagent grade. Absorption spectra were recorded using a Cary-219 spectrophotometer. Singlet and triplet related transient phenomena were studied in a laser flash photolysis set-up consisting of the following: a Molectron UV-400 nitrogen laser system at 337.1 nm., Nd:YAG laser at 266 nm., excimer laser at 248 nm., and a dye laser at 300-350 nm. band, for excitation, a kinetic absorption spectrophotometer with nanosecond response (pulsed 500-W, xenon lamp B&L, UV-Visible high intensity monochromator, and RCA-4840 photomultiplier tube with output signal terminated into 93 ohm), a tektronix 7912 digitizer and SLI-11 microprocessor unit that controlled the experiments and processed the data at the initial stage. The data from LSI-11 were finally transferred to a time shared PDP-11/55 computer system for storage and further treatment. The flash photolysis experiments were carried out on oxygen free, "degassed in the vacuum line", oxygen, air and argon saturated solutions contained in 1×2 cm, quartz cells with the monitoring light passing along the 0.2 cm, path length and the exciting laser light beam intersecting it in the cell at different angles, "between 20°-90°". The concentrations of the solutions were selected 1.54×10^{-5} M, for best signals.

3.Results and discussion

P-type delayed fluorescence, triplet-triplet absorption spectrum and triplet decays in different conditions are reported here. The identity of the delayed fluorescence and prompt fluorescence spectra excludes the possibilty of the triplet state spectra observed being due to an impurity with a low-lying triplet state. Triplet decay times are measured at different wavelengths between 350-500 nm., in ethanol, methanol, benzene and cyclohexane at room temperature for the oxygen, air, argon saturated solutions and vacuum degassed solutions respectively [5,6]. The one photon absorption spectrum in solution at room temperature does display well-resolved vibronic structure. Decay curves for

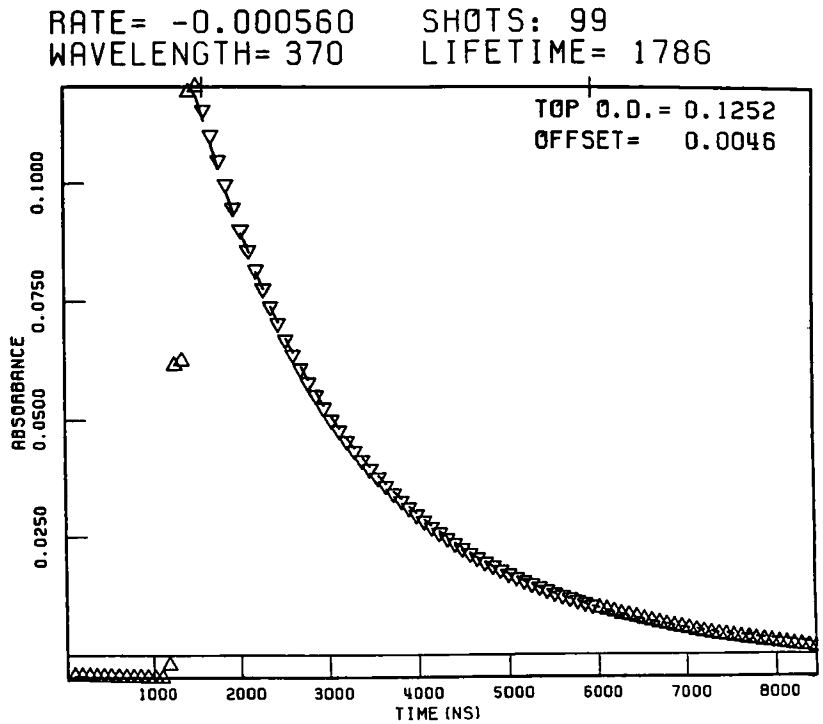

Fig. 2. Triplet decay of vacuum degassed solutions of dibenzothiophene in ethanol at room temperature.

dibenzothiophene triplets recorded between 350-500 nm., were found to follow an experimental decay law: $|^3DBTh|_t = |^3DBTh|_0 e^{-kt}$, where k is a rate constant. Figure 2 shows triplet decay of vacuum degassed solutions of dibenzothiophene in ethanol at room temperature.

Dibenzothiophene triplets are stable at room temperature, this conclusion is rainforced by the appearance of delayed fluorescence. The lowest excited singlet state of dibenzothiophene is regenerated by triplet-triplet annihilation for p-type delayed fluorescence experiments, and decay time is found to be 343

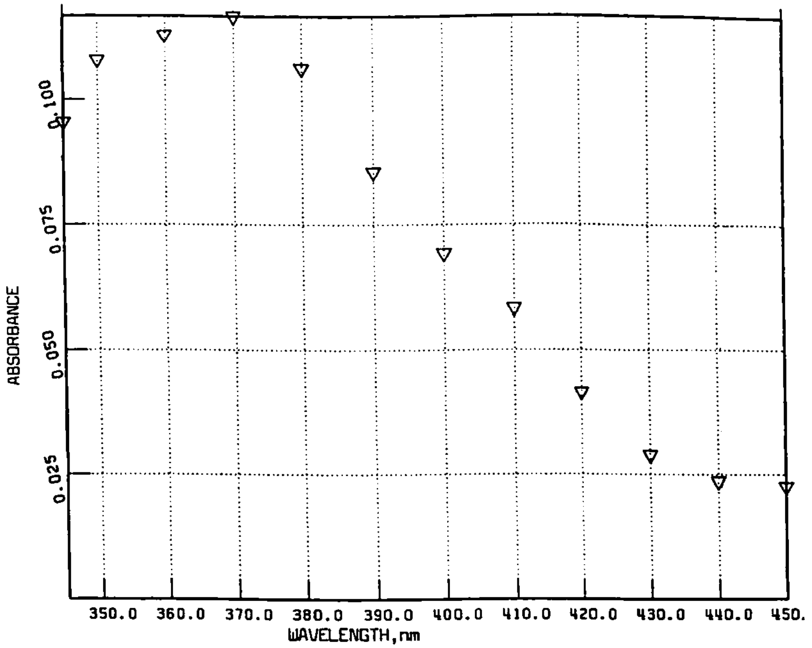

Fig. 3. Triplet-Triplet absorption spectrum of vacuum degassed solutions of dibenzothiophene in ethanol at room temperature.

nsec., in ethanol for vacuum degassed solutions. The measured prompt fluorescence decay time is 6 nsec., Figure 3 & 4 show T-T absorption spectrum and p-type delayed fluorescence decay of dibenzothiophene in ethanol at room temperature respectively. Oxygen is quenched the dibenzothiophene triplets in solution therefore the triplet decay times are found different in different conditions. There is almost no oxygen present when background pressure in the vacuum line was 10^{-7} torr in the solution of dibenzothiophene. For this reason the longest triplet decay time is found for the vacuum degassed solutions and the shortest triplet decay time for the oxygen

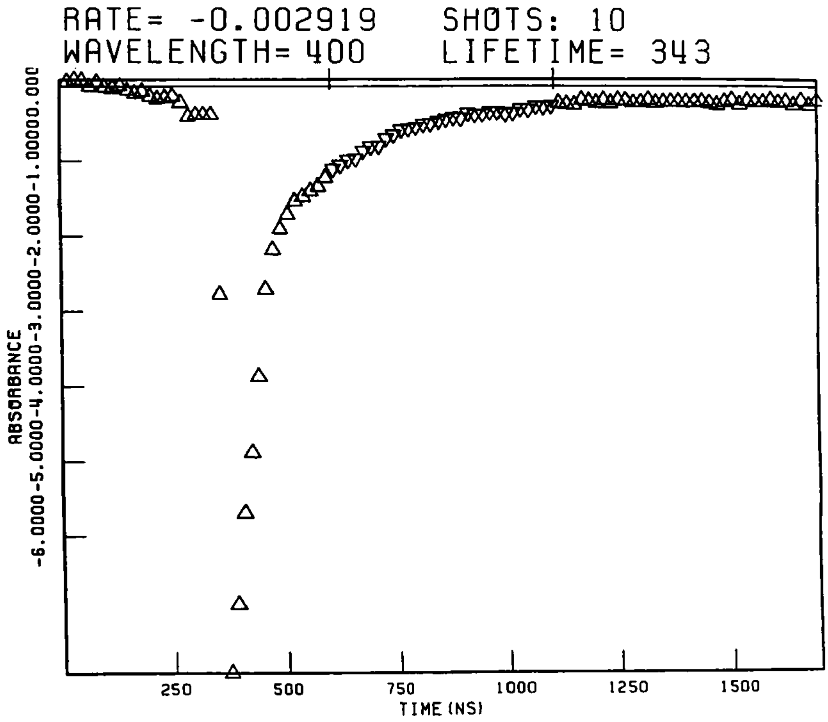

Fig. 4. P-type delayed fluorescence decay of vacuum degassed solutions of dibenzothiophene in ethanol at room temperature.

saturated solutions, "Maximum amount of triplet quenching". Similar results were observed for the rubreneperoxide molecules in solution at room temperature [7] . Two photon of the intense exciting light, at 532 and 600 nm., are absorbed simultaneously in the same quantum act, raising the molecule to an excited state at an energy equivalent to that of two-photons. From it decayed like any excited state to the ground state and the prompt fluorescence lifetimes were found to be the same within the experimental error for one and two-photon excitations. The concentrations of the solutions were

Table 1. Photophysical parameters of dibenzothiophene in different solutions

Solution	Quenching Conditions	T-T absorption peak, nm.	Decay of T_1, ns.	P-type delayed fluorescence,ns
Ethanol	O_2-saturated	370	154	143
	Air saturated	370	167	149
	Argon saturated	370	966	307
	Vacuum degassed	370	1786	343
Methanol	O_2-saturated	370	148	142
	Air-saturated	370	160	155
	Argon-saturated	370	1228	726
	Vacuum-degassed	370	1626	464
Benzene	O_2-saturated	380	188	167
	Air-saturated	380	192	187
	Argon-saturated	380	676	630
	Vacuum-degassed	380	1379	282
Cyclohexane	O_2-saturated	365	175	147
	Air-saturated	365	319	396
	Argon-saturated	365	898	683
	Vacuum degassed	365	1476	379

1.54×10^{-5} M. for all the experiments. Some triplet decay times are reported for different molecules by different authors in the presence of air. Unfortunately there is neither theoretical nor experimental data is present (except ref. 7&8) for oxygen, air, argon, saturated solutions and vacuum degassed solutions of dibenzothiophene-like compounds to compare with our results. Oxygen is a triplet quencher therefore decreasing the oxygen concentration in the solution will increase the triplet decay time of the molecule concerned.

Table 1 shows the decay times of dibenzothiphene in different conditions and in different solutions. Fluorescence emissions and T-T absorption spectra are overlapped around 345 nm., therefore T-T absorption spectrum could be recorded for longer wavelengths than 345 nm. In the one photon absorption spectrum of dibenzothiophene peaks are observed at 195, 211, 233, 236, 255, 263, 279, 281, 287, 313, and 327 nm. The strongest absorption band observed at 236 nm.

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