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High Resolution Optical Spectral Image of the Singlet and Triplet States of Dibenzanthracene in Polymethylmethacrylate

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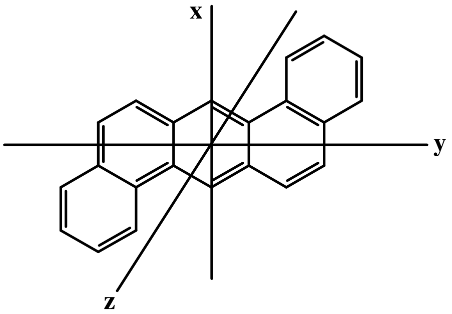
Highly sensitive detection of singlet-singlet, triplet-triplet optical absorptions and delayed fluorescence of 1,2:5,6-dibenzanthracene in polymethylmethacrylate were experimentally observed by flash and laser flash photolysis techniques. 1,2:5,6-Dibenzanthracene molecules were excited in a two-step process. In the first step the excited singlets are created by optical pumping, which undergoes intersystem crossing to triplet state, then triplet-triplet absorption creates an excited triplet 1,2:5,6-dibenzanthracene molecule which returns to the first excited singlet level by intersystem crossing. The re-created first excited singlet of 1,2:5,6-dibenzanthracene decays back to the ground state by emitting B-type of delayed fluorescence, which was observed at the same emission band of normal fluorescence.

Key Words: 1,2:5,6-Dibenzanthracene, Polymethylmethacrylate, Electronic transitions, Delayed fluorescence, Singlet and Triplet decay times.

INTRODUCTION

Dibenzanthracene is white to light yellow crystalline solid, actively carcinogenic cyclic hydrocarbon, $C_{22}H_{14}$ and primarily found in gasoline exhaust, tobacco smoke, coal tar, soot and certain food products, especially smoked and barbecued foods. It is a mutagen and is reasonably anticipated to be a human carcinogen. Polymer matrices are convenient for the study of singlet and triplet related phenomena over a wide temperature range. Such amorphous solids as polymethylmethacrylate remain rigid up to 100 ºC; the temperature dependence of triplet processes has been reported in several polymer matrices. Invariably, the phosphorescence lifetime of aromatic solutes, (larger than benzene) in plastics shortens when the temperature is raised. Above 30 ºC, the triplet lifetime drops precipitated, since the molecular environment is not well defined in polymer matrices, the temperature dependent mechanism remains largely obscure above room temperature. High pressures eliminate diffusional quenching by paramagnetic oxygen molecules in polymer matrix. Therefore, a large pressure dependence of the thermally activated processes is predicted, if the bimolecular quenching is responsible for the diminished phosphorescence at high temperatures. The visible and near ultraviolet absorption spectrum of a centrosymmetric molecule is shifted to longer wavelengths in the presence of an electric field because the polarizabilities of the ground and excited states are different. Excitation spectra of 1,2,:5,6-dibenzanthracene at very high concentrations are characterized by the appear range of broad bands. Decreased lifetimes and marked decrease in quantum yield of the triplet state were observed. The magnetic circular dichroism (MCD) of dibenzanthracene has been measured in the α-absorption region. The sign and magnitude of the MCD observed were in good agreement with those calculated using CNDO wavefunctions. Due to the low vapour pressure of dibenzanthracenes, their vapour phase spectra could not be recorded. B-type of delayed fluorescence was observed experimentally for the first time for rubrene in solution by one and two-photon excitations[1]. Absorption of light raises the molecule from the ground state to one of the upper electronically excited singlet states. At room temperature, most of the molecules are in the lowest vibrational level of the ground state, and it is that upward transitions by absorption of light take place. From the first excited singlet energy level, the molecule can return to any one of the vibrational levels of the ground state with the emission of fluorescence and part of the excited molecules may return to the ground state by other mechanisms, for example, by conversion to the triplet state or by various quenching processes or some may undergo photochemical change. As a result, the fluorescence efficiency is less than unity. From this behaviour, some rules of practical value in qualitative and quantitative spectrofluorimetry can be derived[1-10]. The digital computers are the most powerful tools used in processing experimental data like an image. If an image with a large dynamic range is recorded on a medium with a small dynamic range, such as film or paper, the contrast and therefore the details of the image are reduced, particularly in the bright and dark regions. In fact, the details of small variations on the original analogue spectrum image can be reemphasized by using digital image processing techniques in which an image is digitally formed after the actual scan. On the other hand, increasing the local contrast and reducing the overall dynamic range can significantly enhence the quality of such an image. For this aim, such image enhancement algorithms are required for images after digitization process. On the other side, in some cases, the measurement results exracted from the experimental data might include some measurement noises because of insufficient number of samples. This type of noise can be removed by applying digital filtering techniques like smoothing, averaging[11,12].



Molecular structure of dibenzanthracene

EXPERIMENTAL

The solutes of 1,2:5,6-dibenzanthracene , Eastman Kodak, and other chemicals, Aldrich were chosen for this study at a concentration of 2.5×10^{-4} Molar. The polymethylmethacrylate samples were prepared by thermal polymerization. The singlet and triplet transient phenomena were excited with a flash photoysis set-up consisted of two-parallel photo-tubes arranged in series, contained in a reflector which was flushed with oxygen free nitrogen. The photoflash energies used were 780-1125 J and the flash duration time was two-microseconds. All fused quartz components were spectrosilica grade. The whole spectra, $S_0 \rightarrow S_n$, $S_1 \rightarrow S_0$ and $T_1 \rightarrow T_n$ were recorded on a Hilger medium quartz spectrograph, slit-width 0.025 mm and Ilford XK fast blue sensitive plates sensitized with sodium salicylate and were developed in Ilford PQ universal developer. The spectra were photometered on a Joyce-Loebel double beam recording microdensitometer, Model-MKIIB. Calibrated optical densities on the photographic plate were obtained with a seven-step filter, Hilger F-1273. All kinetic spectroscopy was carried out for single flashes. And the image of the original high-resolution spectra was also scanned by HP Scan-Jet 7400c scanner at 600 dpi resolution to obtain a high resolution digital image. The original spectrum image was transformed to gray level image and normalized by using MATLAB functions. For absorption bands, density information was exracted by inverting the computed averages, replacing the white and black levels of the density information, in order to apply same computational procedure given for emission bands. (Delay times = Times between the discharges of photolysis and spectral flashes).

RESULTS AND DISCUSSION

Absorption of light raises the molecule from the ground state to one of the upper electronically excited singlet states. At room temperature most molecules are in the lowest vibrational level of the ground state and it is from here that transitions upward by absorption of light take place. For many organic compounds the pattern of vibrational levels is complex and all the trasitions to various levels of the first excited state appear as one broad absorption band. From the first excited singlet energy level, the molecule can return to any one of the vibrational levels of the ground state with the emission of fluorescence. The shape of fluorescence emission spectrum is independent of the wavelengths used to excite the molecule, because the emission always takes place from the level S_1. The rate of emission of fluorescence is by definition equal to the rate of light absorption measured in quanta, multiplied by the quantum efficiency of fluorescence. All types of delayed fluorescences involve a metastable state which is first converted to an excitded singlet state before emitting. For this study the molecule 1,2:5,6- dibenzanthracene was especially selected, because its type of symmetry, which allows to a clear-cut polarization assignment, has a singlet lifetime of the order of hundred nanosecond and has a reasonable absorption coefficient at the flash and laser flash excitations wavelengths in the ultraviolet-visible region which means all the transitions are electronic transitions. The triplet states have lower energies than their corresponding singlet states. However, cases are claimed in which S_1 lies below T_1, because of strong coupling between excited states. The solvent or polymer matrix may cause a breakdown of the spin conservation rule for molecules facilitate a charge in multiplicity, and permit weak $S_0 \rightarrow T_1$ absorption to be observed, as it is seen at $T_1 \rightarrow T_n$ absorption band in Fig. 1. However this is not a necessary criterion concerning singlet-triplet mixing. Under favourable conditions, (rigid medium, absence of quenchers), emission of phosphorescence often can compete favourably with delayed fluorescence and intersystem crossing. Although the natural radiative lifetime of phosphorescence is independent of temperature, the actual observed rate of decay of the triplet state is the sum of all competing processes, phosphorescence, intersystem crossing back to the excited state S_1, intersystem crossing to the ground state S_0 and bimolecular reactions with other substances. Dibenzanthracene molecules were excited in a two-step process involving the $S_0 \rightarrow S_1$ and $T_1 \rightarrow T_2$ transitions. Dibenzanthracene molecules in the T_2 state returned to the first excited singlet state "S_1" by intersystem crossing from the excited triplet T_2. The recreated electronically excited S_1 state decayed back to to the ground state S_0 by emitting B-type of delayed fluorescence. The lifetime of B-type delayed fluorescence will be the lifetime of T_2 state, instead of T_1, because the T_2 state is responsible for repopulating the S_1 state of the molecule. The mechanism of B-type of delayed fluorescence was given by Bayrakceken[1].

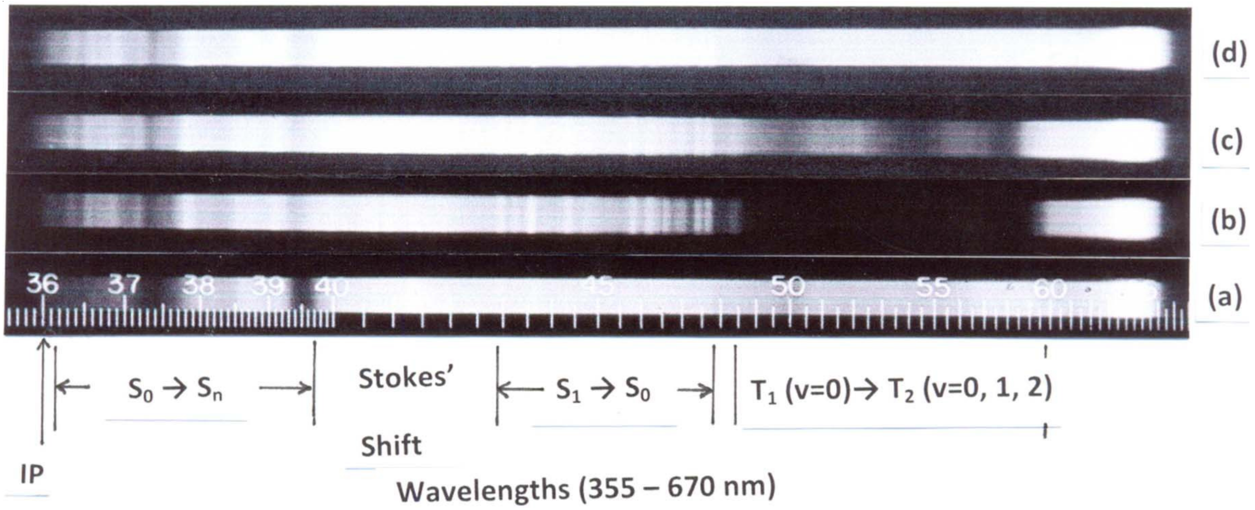


Fig. 1. Singlet-singlet and triplet-triplet absorption spectra and B-type delayed fluoresence spectrum of dibenzanthracene in polymethylmethacrylate (a) Singlet-singlet and singlet-triplet (spin and parity forbidden) transitions of DBA/PMMA; (b) $S_0 \rightarrow S_1$, $S_1 \rightarrow S_0$ and T_1 (v = 0)→T_2 (v = 0,1,2) transitions, delay time = 50 µsec; (c) Same as (b), delay time = 1250 µsec; (d) Same as (b), delay time = 2000 µsec

Continuous absorption started at 360 nm, therefore the first ionization potential of dibenzanthracene *via* singlets was calculated from this edge and found to be 3.44 eV. Due to the very strong continuous absorption below 360 nm, no autoionization discrete energy levels could be observed. The triplet state of dibenzanthracene in polymethylmethacrylate was stable at room temperature and the absorption spectrum was structured,the peaks of triplet state were easily identified at 495, 540 and 580 nm. This conclusion is reinforced by the appearance of E and P type of delayed fluorescences. The identity of the delayed fluorescence and promt (normal) fluorescences spectra excludes the possibility of the triplet state spectra observed being due to an impurity with a low-lying triplet state. Decay curves for dibenzanthracene singlet and triplet states were found to follow an exponential decay law. In order to get best absorption and emission spectra, the concentrations of DBA in polymethylmethacrylate were tested and 2.5×10^{-4} Molar concentration was selected for all flash and laser flash photolysis experiments. In order to measure the decay time of B-type delayed fluorescence, a combination of Kodak glass filters were used between the sample, photolysis flash and spectral flash lamps to eliminate the recombination delayed fluorescence by cutting the emissions of photolysis and spectral flashes. During the optical pumping to create S_1, T_1 and T_2 states, oxygen-free nitrogen was flushed through the optical cavity to keep the temperature constant for the sample. Therefore the possibility of E-type delayed fluorescence was also eliminated. The delay time, between the photolysis and the spectral flash lamps, was selected as hundred nanosecond to eliminate prompt (normal) fluorescence. B-type delayed fluorescence decay time was measured at different emission lines and found to be the same within the experimental error. The best signal was obtained at 436 nm emission line, by using a Tektronix oscillope and decay time of T_2 state to S_0 *via* S_1 state was found to be 270 ± 5 nanosecond, at room temperature in polymethylmethacrylate. The observed long triplet decay times are made feasible merely by inaccessibility from the rigidity of the local microenvironment.

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