

Conclusion

DBPI is more readily reduced than its parent, perylene, due to the electron-accepting nature of the carboximide substituents in DBPI. The three electron-transfer products of DBPI examined in this paper, DBPI^{•-}, DBPI^{•+}, and DBPI²⁻, have intense absorption bands in the visible or near-infrared region that make them easy to identify spectroscopically. Practical applications of

DBPI or analogous dyes as photosensitizers may be limited to singlet excited-state reactions because of the expected low reactivities of their triplet excited states.

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Photophysical Processes of Polymethine Dyes. An Absorption, Emission, and Optoacoustic Study on 3,3'-Diethylthiadodicarbocyanine Iodide

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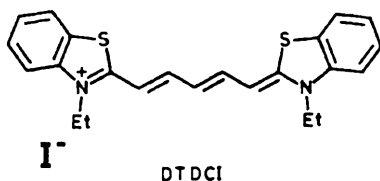
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Laser flash photolysis, laser-induced optoacoustic spectroscopy (LIOAS), and fluorescence data were used for the study of the photophysical deactivation processes of excited 3,3'-diethylthiadodicarbocyanine iodide (DTDCI). Direct excitation of this molecule in air-saturated methanol solutions at room temperature results in the formation of only one transient species, a photoisomer, the spectrum of which was derived for the 600-680-nm spectral range. The energy content difference between the ground state of the stable form and that of the photoisomer was evaluated, $\Delta E = 0.15 \pm 0.15$ eV, as well as limit values for the photoisomer fluorescence quantum efficiency ($\Phi_F^P < 0.2$) and for the quantum yield for the back-photoisomerization from the first excited singlet state of the photoisomer to the ground state of the stable form ($\Phi_{PN} \leq 0.14$).

Introduction

3,3'-Diethylthiadodicarbocyanine iodide (DTDCI) is known as a laser dye for pulsed operation in the region 700-760 nm and as a saturable absorber for mode-locking, when used with cresyl violet and rhodamine 101 lasers.^{1,2}



Similar to the case of other cyanine dyes, evidences for a reversible photoisomerization process, produced by irradiation with high fluences, have been reported.³⁻⁶ The lasing and saturable absorption properties of DTDCI are probably closely related to the absorption and emission spectra of the photoisomer (P).

The photoisomerization processes and the general photophysical properties of DTDCI are not sufficiently well-known; e.g., the possibility of the existence of more than one transient species has been postulated.⁴

Conventional and laser flash photolysis experiments have been carried out by various groups. Dempster et al.³ reported the existence, in ethanol solutions, of a photoproduct, P, and calculated possible limits for its absorption coefficient. Kalitetskaya and Razumova⁴ reported that the transient changes in transmission were different for excitation with UV light at 347 nm than for excitation with red light (690 nm). As a consequence, they proposed the existence of two isomers, one (P) generated from the first excited state of the stable form (N) and a second one (M) generated from the first excited state of P. The absorption spectrum calculated for P in this work was quite different from the limits calculated by Dempster et al.³ Fluorescence studies in different solvents including methanol, performed by exciting

with UV light, did not need the postulation of a second photoisomer.⁷ Thus, the accepted photoisomerization mechanism through a twisted state, similar to that proposed by Rullière for the photoisomerization of DODCI,⁸ was postulated.⁷ In addition, there are various values in the literature for the quantum yield of photoisomerization, Φ_{NP} , from 0.015 to 0.5.^{3,4,6}

Laser flash photolysis, laser-induced optoacoustic spectroscopy (LIOAS), and fluorescence measurements were used in this work to study the deactivation processes taking place upon excitation of DTDCI in methanol. By means of a simple numerical model to analyze the kinetic processes, the absorption spectrum of P is determined and values for the deactivation parameters of the photoexcited isomer are calculated.

Experimental Section

The experiments were made in methanol-aerated solutions at room temperature. In order to minimize dimerization effects, excitation was always performed with dilute ($\leq 10^{-6}$ M) samples. Methanol was chosen among the alcohols due to the higher stability of the dye in this solvent. The absorption properties of DTDCI in methanol are essentially the same as in other types of organic solvents.

DTDCI was used as supplied by Eastman Kodak. Methanol (Merck) was used as purchased. Absorption spectra were measured with a Cary Model 14 and a Perkin-Elmer Model 356 spectrophotometers. Corrected fluorescence spectra were taken

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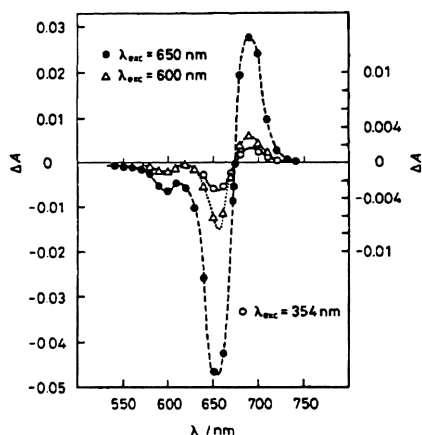


Figure 1. Absorption changes, ΔA , immediately (15 ns) after the excitation of an aerated 10^{-6} M DTDCI/MeOH solution at different excitation wavelengths. The scale on the left corresponds to $\lambda_1 = 650$ nm and 600 nm. The scale on the right corresponds to $\lambda_1 = 354$ nm.

at 20 °C with a Spex Fluorolog spectrofluorimeter. Rhodamine 101 ($\Phi_f = 1.0^9$) and cresyl violet ($\Phi_f = 0.54^{10}$) were used as references. The solutions of sample and references had matched absorbances at the respective excitation wavelengths. The two references lead to the same fluorescence quantum yield for DTDCI in methanol, $\Phi_f = 0.36 \pm 0.05$, in agreement with the literature data.¹¹ No corrections for the refractive index difference between methanol and the solvent used for the reference (ethanol) was made.

The nanosecond flash photolysis equipment with optical detection was already described.¹² It consists of a Nd:YAG laser (15-ns pulse duration) either in its third harmonic at 354 nm or when pumping dye lasers (R6G and DCM, Lambda Physik), in its second harmonic at 532.5 nm. The transient absorbance changes were monitored at 90° with respect to the excitation for periods of 1 ms with the pulsed beam of a 150-W Xe arc lamp. The laser energies employed were on the order of 3 mJ for all the measurements. Signal acquisition was performed with a computer-controlled Biomation Model 4500 transient recorder. Signal averaging and handling was performed with an LSI 23/VAX 780 computer system.

The experimental setup for LIOAS was the same as used in ref 13. The excitation source was a flash-lamp-pumped dye laser (Chromatix Model CMX-4). Rhodamine 6G (Exciton) in methanol/water was used for the range 580–620 nm and rhodamine 640 for the region 630–690 nm. The laser beam (1- μ s pulse duration, maximum energy 1 mJ, repetition rate 2 Hz), after focusing and passing through a diaphragm, had a diameter of 1 mm ($1/e$ of the maximum intensity) in the sample cuvette. The resolution time of the whole system was 1 μ s.¹³ In these experiments, CuCl_2 in methanol was used as a calorimetric reference. Absorbances of DTDCI and those of the reference were matched to ± 0.005 AU.

Results

Flash Photolysis. The transient absorption changes, ΔA , determined after excitation at 354, 600, and 650 nm are shown in Figure 1. The main characteristics observed immediately after the pulse are a difference absorbance minimum at 655 nm, a maximum at 690 nm, an isobestic point at 675 nm, and a small absorbance decrease in the range 600–630 nm.

The general features of the differential spectra are similar to those reported previously^{3,4} for excitation in the orange-red region

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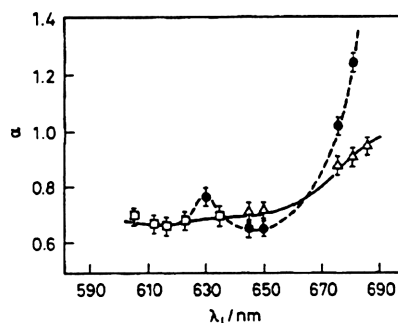


Figure 2. Action spectrum of prompt heat dissipation (α) from photoexcited DTDCI at $\lambda_1 = 605, 612, 617, 625, 630, 645, 650, 675, 680,$ and 685 nm. Key: excitation energy, (Δ) 10 μ J and (\bullet) 100 μ J; \square , isooptoacoustic points. The fit with the mathematical model gives the full and dashed lines for low and relatively higher energies for the values $\Phi_{NP} = 0.5$, $\Phi_{PN} = 0.14$, and $\Delta E = -0.15$ eV.

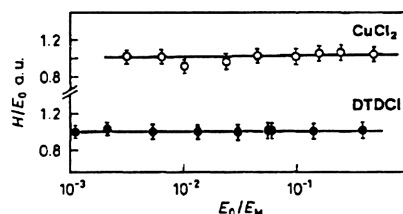


Figure 3. Energy dependence of the normalized heat emission H/E_0 for an isooptoacoustic point for solutions DTDCI/MeOH and $\text{CuCl}_2/\text{MeOH}$ at the same absorbance ($A = 0.12$) at $\lambda_1 = 610$ nm. Maximum laser pulse energy, $E_M = 150$ μ J.

but different for excitation in the UV region. We found an isobestic point at $\lambda = 675$ nm, independent of the excitation wavelength in contrast to the reports by Kalitetskaya and Razumova.⁴ The first-order plot of the decay of the absorption was identical for various detection wavelengths and yielded a rate constant $k = (3.9 \pm 0.7) \times 10^3$ s⁻¹. This value is similar to that obtained by Dempster et al., using laser flash photolysis ($k = 4.1 \times 10^3$ s⁻¹),³ and somewhat higher than that obtained by Kalitetskaya and Razumova after excitation with red light ($k = 2.77 \times 10^3$ s⁻¹).⁴

LIOAS. As it is usual in these types of experiments,^{13,14} the maximum of the amplitude of the first acoustic signal generated after the absorption of the laser pulse was measured for sample (H_{DTDCI}) and reference (H_{CuCl_2}) under the same experimental conditions. The prompt heat, dissipated during the time window of the experiment (1 μ s), for different wavelengths and energies of excitation is calculated as $\alpha(\lambda) = H_{\text{DTDCI}}/H_{\text{CuCl}_2}$. The ratio α was determined for the region 605–680 nm (Figure 2). For each wavelength, the initial absorbances of the sample and reference were matched. Figure 2 shows the dependence of α with the excitation wavelength for two values of constant excitation energies ($E_M = 100$ and 10 μ J).

The results of Figure 2 can be discussed taking into account the expected signal vs wavelength dependence for a system without an energy-storing species. In such a case, the heat dissipated promptly would have a constant value, independent of excitation wavelength and energy. In our case, as the excitation energy is increased, there is less heat emitted for the region 635–665 nm, while, on the contrary, above 665 nm there is more heat released to the medium than expected. In the region 605–625 nm and at $\lambda = 635$ nm, $\alpha = 0.67 \pm 0.05$ was obtained independently of the excitation wavelength and energy. In addition, for this region, the amplitude H_{DTDCI} of the acoustic signal was measured as a function of the energy of the exciting pulse (E_0) in a range of 3 orders of magnitude. The energy-normalized heat emission (H/E_0) for the sample and reference plotted as a function of E_0

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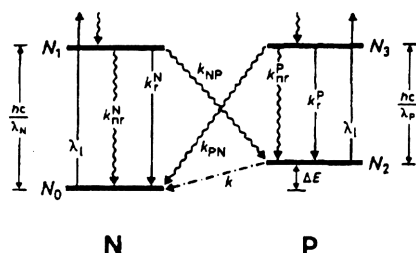


Figure 4. Scheme showing the stable (N) and isomeric (P) forms of DTDCI and the rate constants for the different processes interconnecting both species. The wavy lines represent the processes dissipating heat within the time window of the experiment. See text for the explanation of symbols.

shows no dependence with the energy. Figure 3 shows an example for the case of excitation at 610 nm.

Discussion

The results of flash photolysis show the existence of one transient species that thermally returns to N with a rate constant $k = (3.9 \pm 0.7) \times 10^3 \text{ s}^{-1}$. We identify this transient with a photoisomer (P) of N on the basis of the similarity of the spectral difference between these species with those described for the photoisomers of other cyanine dyes (e.g., DODCI³). No evidence of other transient species was found at room temperature under our conditions. Thus, the model and the equations employed in ref 13 for the photoisomerization processes of DODCI can be used to analyze the LIOAS results and to evaluate kinetic and spectroscopic parameters of the photoisomerization of DTDCI. Figure 4 shows the scheme employed.

Since $\Phi_{ISC} < 10^{-2}$ was evaluated for DTDCI in ethanol and a series of solvents^{3,6} the triplet was not considered in the scheme.

k_{NP} and k_{PN} are the rate constants for isomerization of $N \rightarrow P$ and $P \rightarrow N$ from the excited states, k is the rate constant for the thermal $P \rightarrow N$ isomerization, and k_r^N , k_r^P , k_{nr}^N , and k_{nr}^P are the rate constants for radiative and nonradiative decay from excited N and P, respectively. λ_1 is the laser wavelength and λ_N and λ_P are the wavelengths for the 0-0 transitions for N and P, respectively. ΔE is the difference in energy content between N and P.

At the low concentrations used in this work, it is reasonable to assume that radiative or Förster energy-transfer processes between both species can be ruled out, as well as the formation of aggregates.

When DTDCI, initially is in its stable form (N), is excited with microsecond pulses, a phototransformation from N to P (lifetime of excited N, $\tau_1 = 1.38 \text{ ns}^{15}$) takes place. At fluence rates $\geq 1 \text{ kW/cm}^2$ and with the strong overlap of the absorption spectra of both species being taken into account, a photochromic system between N and P should be built within the laser pulse duration as suggested by Dempster et al.³ The energy dependence of the signal (Figure 2) at different λ_1 shows a behavior similar to the one we found for DODCI,¹³ which was explained also by the establishment of a photochromic equilibrium between N and P within the laser pulse duration. The transient bleaching of the sample observed in flash photolysis (Figure 1) and the loss of heat at higher energies in the LIOAS experiments for wavelengths below 665 nm (Figure 1) is thus attributed to the formation of P, which does not thermally return to N during the pulse duration (lifetime of P, $\tau_2 \approx 260 \text{ ps}$). With the excitation energy in LIOAS experiments being increased, less N is available for the process and the value of α is reduced. For $\lambda_1 > 665 \text{ nm}$, corresponding to the region where the absorption of P becomes important (Figure 1), the increase of the heat emission at higher energies (Figure 2) is due to an increase in the absorbance of the sample during the pulse as a consequence of the buildup of P. It is then reasonable to support the concept that the fluorescence quantum yield

of P should be smaller than that of N, in agreement with the proposal by Enikhen and Berezovin.⁵

The lack of dependence of α with the laser energy in the 605–625-nm region and at $\lambda = 635 \text{ nm}$ indicates that these are isoptoacoustic points defined as the wavelengths at which the total energy emitted by the sample as heat does not change upon a chemical or physical perturbation.^{16,17} In these points

$$\sigma^N \alpha_N = \sigma^P \alpha_P$$

where σ^N and σ^P are the absorption cross sections of N and P at λ_1 and α_N and α_P the nonradiative efficiencies of N and P, respectively. The presence of isoptoacoustic points is further demonstrated by the lack of dependence with laser energy of the normalized heat emission for these wavelengths (Figure 3). Consequently, care should be exercised when analyzing energy dependences of optoacoustic signals, since linear dependencies do not necessarily imply the lack of an additional absorbing species in the system. Extended isoptoacoustic regions may be present in a four-level system.

At very low excitation energies, the population N_2 is negligible with respect to N_0 , and the only species absorbing is N. Thus, at the isoptoacoustic points, $\alpha = \alpha_N = 0.67 \pm 0.05$ (from Figure 2). Taking into account the scheme of Figure 4, energy balance considerations lead to

$$\frac{N_A hc}{\lambda_1} = \Phi_f^N \frac{N_A hc}{\lambda_f} + \alpha_N \frac{N_A hc}{\lambda_1} + \Phi_{NP} \Delta E \quad (1)$$

Φ_f^N and Φ_{NP} are the quantum yields of N fluorescence and $N \rightarrow P$ photoisomerization, respectively; λ_f is the wavelength of the fluorescence maximum of N, h is the Planck constant, N_A is the Avogadro constant, and c is the speed of light. With our value of $\Phi_f^N = 0.36$

$$\Phi_{NP} \Delta E = 7.2 \times 10^3 \text{ J mol}^{-1} \approx 0.075 \text{ eV} \quad (2)$$

is obtained. This value represents the middle point between extremes calculated for various combinations of λ_1 (isoptoacoustic points, between 605 and 630 nm) and λ_f and the values for α_N and Φ_f^N with their respective errors. Thus, the range for the product $\Phi_{NP} \Delta E$ is $\pm 100\%$.

From the same analysis with the same nomenclature as in ref 13, the system of rate equations describing the time evolution of the populations of the states (see Figure 4) can be solved, employing a fourth-order Runge–Kutta numerical method. The heat released promptly by DTDCI and the reference is thus calculated, and the values for α vs λ_1 are obtained, fitting this way the experimental data.

The literature value for the lifetime of excited P, $\tau_3 = 0.27 \text{ ns}$,¹⁸ and $\Phi_f^N = 0.36 \pm 0.05$ (see Experimental Section) were used. Three values for $\Phi_{NP} = 0.5$,⁶ 0.12,³ and 0.03^{3,4} were tried with the corresponding ΔE values from 2, and $0 \leq \Phi_f^P \leq 0.2$ (as suggested in ref 5) were used. The fitting parameters adjusted for the points of Figure 2 were as follows: $B = \sigma^P / \sigma^N$ and Φ_{NP} and $\Phi_{PN} = k_{PN} \tau_3$. In the region of 605–650 nm, the parameter largely affecting the fit is B , especially at the isoptoacoustic points. Changes in the other parameters do not produce important modifications. For the region 650–690 nm, several combinations of the fitting parameters can be used. However, in the isobestic point, determined by flash photolysis at $\lambda_1 = 675 \text{ nm}$, $B = 1$ and the best fits for 10 and 100 μJ were obtained with $\Phi_{NP} = 0.5$, $\Delta E = 0.15 \pm 0.15 \text{ eV}$ (eq 2), and $\Phi_{PN} \leq 0.14$. With these values, B was then adjusted for the whole spectrum and good fits were obtained for low and relatively high energies as shown in Figure 2.

Figure 5 shows the spectrum of P deduced from the calculated values of B , together with the spectrum of N. The spectrum determined for P is within the limits calculated in ref 3.

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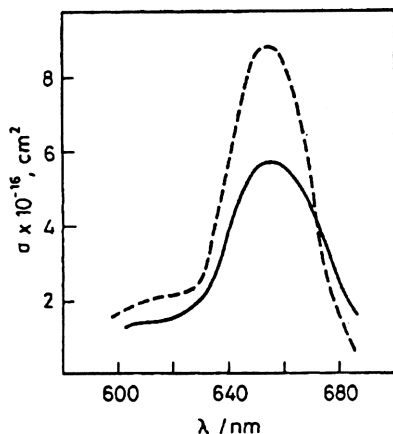


Figure 5. Absorption spectra of the most stable isomer N (---) and the photoisomer P (—) of DTDCI. The latter spectra is derived from the optoacoustic measurements (see text).

The strong superposition of the spectra in both isomers was also confirmed by means of fluorescence measurements. With DTDCI being excited at 650 nm with the flash-lamp-pumped dye laser and various fluences (from 8.5 to (4×10^3) kW/cm²) being used, no changes were observed in the emission spectra, with respect to conventional fluorescence measurements.¹⁹ For the same conditions of excitation, other cyanine dyes, for which the absorption spectra of both isomers are not so strongly superimposed, show important variations in the fluorescence spectra, depending on the wavelength and excitation energy, due to the emission of both species.²⁰

The evaluation of the photophysical parameters for the photoisomerization of DTDCI is less precise than for the case of DODCI,^{14,16} a cyanine dye with the same polymethinic chain but just a different heteroatom (S instead of O) in the final rings. Some general conclusions can be extracted. Similar to the case of DODCI, the fluorescence quantum yield of the excited isomer of DTDCI seems to be lower than that of excited N and the photoisomerization of N to P is more efficient than the back-photoisomerization P* \rightarrow N. The latter result can be discussed, taking into account that the accepted scheme for the isomerization mechanism of these molecules follows the normal double bond photoisomerization through a twisted intermediate. This was proposed for the case of DODCI, for which twisting constitutes the main radiationless deactivation channel for the excited N,⁸ while internal conversion without passing through the twisted state is the main deactivation channel for excited P.¹⁶ This conclusion was derived from the fact that the branching ratio from the twisted state to N and P has to be the same, independent of the origin

of this state, and has been later confirmed by Rentsch et al.²¹ and Zhu and Harris.²²

For the case of DTDCI, the situation cannot be defined so accurately. When, in analogy with DODCI, no direct internal conversion from excited N is assumed and a value $\Phi_{NP} = 0.5$ is used, a value of 0.8 is obtained for the branching ratio to P from the twisted state, when it is arrived from excited N. This value is the same as that from excited P with use of $\Phi_{PN} = 0.14$. This means that, under this assumption, in this case excited P deactivates by passing through the twisted state. However, it is not clear yet that this assumption is valid for DTDCI. More data, especially temperature-dependent photoisomerization quantum yields, are needed to completely understand the mechanisms of deactivation of excited N and excited P in DTDCI.

Additional differences between DTDCI and DODCI are as follows: (i) In the former, the ground state energy of P is much lower than in the latter; i.e., it is only slightly above N. (ii) The spectra of N and P overlap more for DTDCI than for DODCI.

Conclusions

The photophysical behavior of DTDCI can be explained in terms of a reversible photoisomerization process between two configurational isomers. No evidence was found for the presence of an additional isomer in methanol as had been suggested by Kaliteevskaya and Razumova.⁴

Using LIOAS and a simple scheme connecting the stable form and its photoisomer, we can calculate the absorption spectrum for the photoisomer and limits for its fluorescence quantum yield ($\Phi_f^P < 0.2$) and the quantum yield for back-photoisomerization from the first excited singlet state of this species to the ground state of the stable form ($\Phi_{PN} \leq 0.14$).

The application of LIOAS to the study of this system has resulted in a better resolved absorption spectrum of both species than that resulting from conventional and laser flash photolysis. No region shows absorption of one species alone, and it is not possible to use the method developed in ref 16 to obtain the energy content of the less stable isomer. Fitting the photoacoustic data permitted us to estimate $\Delta E = 0.15 \pm 0.15$ eV. The use of the data at the isoptoacoustic points has led to the evaluation of spectroscopic and kinetic parameters of a photoisomer with optical properties very similar to those of the parent compound. This further demonstrates the potential of the LIOAS technique.

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