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Triplet Extinction Coefficients of some Organic Compounds

by

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ABSTRACT
The triplet extinction coefficients $\epsilon_T$ of acridine, anthracene, benzanthracene, dibenzanthracene, chrysene, pyrene, and pyrene-carboxaldehyde were measured at the visible spectral region at maximum triplet-triplet absorption. We used McClure's method together with cw lasers as excitation sources to obtain the $\epsilon_T$ values. Because these triplet extinction coefficients were measured with improved accuracy, we suggest that these compounds be used as standards. We wanted to compare the accuracy of our values with the ones suggested as tentative standards. Further, we tested the validity of McClure's method on anthracene by increasing the cw laser excitation intensities (power) $I_{ex}$ and recording triplet optical densities $OD_T$. Under the experimental conditions we used, about 100 mW of cw laser power appears to be the upper limit.
Inroduction

Visible/UV absorption spectroscopy of organic compounds is widely used to characterize the physical as well as chemical properties of organic compounds.

In chemistry, absorption spectra of organic compounds are generally presented as extinction coefficients and expressed in $\ell$/mole cm. These (conventional) absorption spectra are referred to as singlet-singlet (S-S) absorption spectra. Here, the molecule has its two outer-orbit electrons with their spins aligned antiparallel with each other. The corresponding triplet-triplet (T-T) absorption spectra, where the two outer electrons are aligned parallel with each other, have not been as widely studied. In a recent review paper on T-T absorption spectra of organic compounds in condensed phases, Carmichael and Hug [1] listed only 1143 compounds in which triplet optical densities $OD_T$ and triplet extinction coefficients $\alpha_T$ (about 30% of the total number) had been measured. These data were obtained by using different excitation sources and seven different methods for measuring triplet extinction coefficients. Each of these methods has its own range of measurement accuracy and sensitivity. Advantages, disadvantages, limitations, etc., for each of the seven methods are discussed in detail.

Some of the methods employed to obtain $\alpha_T$ values are not too accurate, and one observes a rather wide variation for $\alpha_T$ values. From the 1143 compounds listed, Carmichael and Hug selected 32 of the most widely studied (measured) compounds. A rather exhaustive
statistical analysis was performed and the 95% confidence intervals (c.i.) of the average \(<\langle T \rangle\) values (tentative standards) were calculated and also listed in Table 5 of ref. 1 (referred to as Table 5 in this text).

Over the last few years, we have reported \(\epsilon_T(\lambda)\) values on organic compounds, including many laser dyes [3,4]. We employed the intensity variation method introduced by McClure to obtain \(\epsilon_T(\lambda)\) values [5]. The lines from cw lasers were used as excitation sources [6,7]. This combination, in our opinion, results in the simplest as well as most accurate method for obtaining \(\epsilon_T(\lambda)\) values. From the 32 organic compounds listed in Table 5, we selected those that had the following characteristics: most strongly absorbed the cw laser UV lines we had available, were of good photostability under UV cw laser excitation, and showed strong T-T absorption. It should be noted that all the compounds we used have a rather long triplet state (phosphorescence lifetime) \(\tau_T\), ranging from a fraction of a second to seconds. Because of their strong T-T absorption over the spectral region studied, together with good photochemical stability, these compounds are among a rather small number of compounds in which the triplet extinction coefficients are most easily measured and, consequently, these compounds are those that have been most widely studied. We believe that our \(\epsilon_T\) values for the compounds we studied are an improvement in accuracy compared to the tentative standards, i.e., the statistical values (average\(\langle\rangle\) \(<\langle T \rangle\) shown in Table 5.
a. Spectroscopic Equipment and Experimental Procedures

The same equipment and experimental procedures as described in [2] were employed. We present the experimental arrangement in Figure 1. The sample $S$ is submerged in liquid nitrogen (dewar LND). The triplet-state lifetime $\tau_T$ of organic compounds is much longer in a solid than in a liquid solution. Therefore, to generate high concentrations of triplet-state molecules $N_T$, organic compounds are dissolved in a solvent (the glassy solvent) that forms a glassy solid at liquid nitrogen temperature. A cw laser is focused on the sample $S$ with the aid of the lens $L_3$, generating high a concentration of triplet-state molecules $N_T$. For excitation, we used the laser lines at $\lambda_{CW} = 351.1/363.8$ nm from a Spectra Physics model 2025-05 cw argon-ion laser or $\lambda_{CW} = 325$ nm from a Liconix He/Cd cw laser. The monitoring (probing) light MLS was an Oriel model 6341 point source lamp. The measurements consisted of recording four triplet optical densities $OD_T$ as functions of different excitation intensities (power) $I_{ex}$ of the laser beam. The power $I_{ex}$ was recorded with a laser power meter PM from Liconix (model 45 PM). The measurements were performed at the wavelength of maximum T-T absorption, as listed in Table 5. One plots $1/OD_T$ versus $1/I_{ex}$ and extrapolates to the ordinate to obtain $1/OD_T^\infty$. After $OD_T^\infty$ has been determined, according to McClure's method, only the thickness $d$ of the sample and the concentration $N_S$ has to be known. The following simple relationship holds:

$$\tau_T = \frac{OD_T^\infty}{N_S} \cdot d.$$  \hfill (1)
Because measurements are made at the temperature of liquid nitrogen, besides the contraction factor $\rho$, one has to guard against saturation. The solubility of an organic compound in a glassy solvent at room temperature might be rather high. However, by cooling the solution to the temperature of liquid nitrogen, solubility in the glassy solid is very often considerably reduced. We used the following general rule: For each compound, we measured the $\epsilon_T$ values at two different concentrations [2-4]. Starting with two different concentrations, say $A > B$, and cooling to liquid nitrogen temperature, there are three cases to consider: (1) The unknown saturation concentration is lower than both $A$ and $B$. In this case, one would observe the same triplet optical density $ODT_\infty$ for both concentrations. This is because the saturation concentrations would be the same. In the case, (2) not $A$, but $B$ is lower than the saturation concentration. The obtained $\epsilon_T$ value for the $A$ concentration would be smaller than the $\epsilon_T$ value obtained from the $B$ concentration. This is simply the result of Eq. (1). In the case, (3), if both concentrations $A$ and $B$ are below the saturation concentration, one should measure $\epsilon_T$ values that are about the same.

b. Chemicals

Acridine, 99%; anthracene, 99.9% Gold Label; 1,2-benzanthracene, 99%; 1,2,5,6-dibenzanthracene, 97%; chrysene, 95%; pyrenecarboxaldehyde, 99%; and methanol, spectroscopic grade, were obtained from Aldrich Chemical Company. Pyrene was obtained from Eastman Kodak and several times zone-refined. 2-methyl-
tetrahydrofuran was purchased from Lancaster Synthetic Ltd., and ethanol (190-proof punctilious) from Quantum Chemical Ltd., USI Division.

RESULTS AND DISCUSSION

a. Triplet Extinction Coefficients

To provide some information on measurement reproducibility, we present in Table 1 $\alpha_T$ values and their averages for two different concentrations of pyrene. For every concentration, we made three separate experimental runs and present each of the three $\alpha_T$ values together with the mean square error. Each of these values were obtained by varying $I_{ex}$ by a factor of four to measure the corresponding $1/OD_T$ and extrapolating $1/I_{ex} \to 0$, to obtain $1/OD_T$. Each $OD_T$ was measured twice. The $\alpha_T$ value obtained with the $2 \times 10^{-4}$ molar solution was discarded, because it is somewhat lower than the one obtained with the lower concentration. It is not shown in Table 2.

In Table 2 we present all the $\alpha_T$ values for the organic compounds we measured. Again, each value is the average of three $\alpha_T$ values, together with the mean square error.

In all our measurements, we always discarded the $\alpha_T$ values obtained at the $2 \times 10^{-4}$ molar concentrations, because the resulting $\alpha_T$ values were always lower than the ones obtained at $1 \times 10^{-4}$ molar. The only exceptions were anthracene and chrysene, were we had to go as low as a $5 \times 10^{-5}$ molar solution to stay below the saturation concentration. In some cases, where the $\alpha_T$ values taken at the higher concentration were only some
what smaller, but within measurement error, we still enforced the above criteria and discarded the values.

In Table 2 we also present the highest cw laser power $I_{ex}$ used for excitation to obtain the highest $OD_T$ (smallest $1/OD_T$) value and the corresponding fraction in percent of triplet-state molecules of $N_T$ generated. For example, for acridine, 10.0 mW of cw laser power $I_{ex}$ would convert 73% of the original molecules into triplet-state molecules $N_T$. However, the highest cw laser power $I_{ex}$ employed was strictly determined by the lowest laser power $I_{ex}$ necessary to obtain the lowest $OD_T$ value. In this case, $I_{ex} = 2.5$ mW (yielding the point 0.4). This power was sufficient to generate an $OD_T$ value that was considerable above the noise level ($I_0/I$ about 2) of the monitoring light intensities. The noise level of $I_0$ was about ±1 to 2%. The next $I_{ex}$ value was 3.3 mW (yielding the point 0.3), then $I_{ex} = 5$ and 10 mW (yielding the points 0.2 and 0.1, respectively). As indicated, one extrapolates to the point $1/I_{ex} = 0.0$ to obtain $1/OD_T^∞$.

Our $ τ_T $ values shown in the Table 2, according to the measurement error estimation given in [4], should be within ±10 to 15%. As mentioned before, a careful evaluation of the accuracy of the different experimental methods to measure $ τ_T $ values is provided in [1], and we do not repeat the evaluations. We only wanted to present our data side-by-side with the tentative standard $ <τ_T> $ values shown in Table 5.

In the Table 2, our $ τ_T $ value for acridine is 14% lower than the one listed in Table 5, but stays within the 95% confidence
interval (c.i.). For anthracene, our \( c_T \) value is 15% higher. There may be two possible reasons for this discrepancy: (1) Our measurements were performed at the liquid nitrogen temperature, whereas the value listed in Table 5 is the average of different measurements, some of them taken at room temperature. Room temperature measurements yield broader T-T absorption spectra with lower values for the intensity maxima. (2) Some of the measurement may have been performed at low temperatures with concentrations possibly above the saturation point.

In Figure 2A, we present a typical \( 1/I_{ex} \) versus \( 1/OD_T \) (presented as crosses) plot for anthracene. The highest-power \( I_{ex} \) used is 2 mW (the point 0.5), and the lowest is 0.5 mW (the point 2.0). The extrapolated \( 1/OD_T^\infty \) value is 0.66 or \( OD_T^\infty = 1.52 \), which presents a 100% conversion of the original concentration \( N_S \) into triplet-state molecules \( N_T \). At 2 mW, we have \( OD_T = 0.76 \), presenting a 50% conversion ratio of singlet-state molecules \( N_S \) into triplet molecules \( N_T \). The 2 mW are sufficient to extrapolate to the ordinate and to obtain a reasonable accurate \( 1/OD_T^\infty \) value. One can also say that the smallness of the \( I_{ex} \) values used for producing the smallest \( 1/OD_T \) value is a measure of how easily (efficiently) one generates triplet-state molecules \( N_T \) of a compound. As a general rule, one uses the lowest-excitation power \( I_{ex} \) possible in order to keep photodecomposition to a minimum. Anthracene is an exceptional case. In the glassy solvent we employed, it is among the most photostable compounds we studied.
Our $\chi_T$ value of 91.5 listed in Table 2 agrees with $\chi_T = 88 \times 10^{-4} \, \text{l/mole cm}$ (wrongly listed as $82 \times 10^{-4} \, \text{l/mole cm}$) in [2]. Our $\chi_T$ value of benzanthracene is 14% higher than the one listed in Table 5, and again within the c.i. In addition, the dibenzanthracene $\chi_T$ value is 13% lower than the one in Table 5, but again falls within the c.i. The $\chi_T$ value we obtained on chrysene agrees well with the one listed in Table 5. The $\chi_T$ value we reported for pyrene is about 20% lower than the one listed in Table 5 and the one reported in [2]. Pyrenecarboxaldehyde yields an $\chi_T$ value that is about 20% lower than the one listed in Table 5 and does not fall within the c.i.

b. Experimental Limits of McClure's Equation

When exciting organic compounds with intense light into their spectral regions of absorption, and depending on the experimental conditions (solid, liquid, or gas phase), the following effects are often observed: One may detect from some to a considerable number of molecules present in their lowest triplet state $T_1$. One will also observe various amounts of photodecomposition, which is generally the result of first generating radicals, which react further to produce photoproducts. The question we are concerned with is the following: When does McClure's method break down? The higher the excitation intensity (power) $I_{ex}$, the higher the number (concentration) of triplet-state molecules $N_T$ generated. This allows one to come closer to the ordinate, and the more accurate the extrapolation to $1/I_{ex} \rightarrow 0$ will be. Ideally, if, at a certain $I_{ex}$ power level, one could transform,
say, 98% of all molecules into the triplet state, one actually would not need to use McClure's method. With 2% error, the recorded $OD_T$ value is practically the same as the extrapolated $OD_T^{\infty}$.

However, performing experiments at higher excitation intensities $I_{ex}$, one always observes increased photodecomposition. In addition, triplet-singlet backtransfer may occur. At a certain power level, melting of the sample and/or blooming is also observed. To obtain some quantitative data on the limit of the power $I_{ex}$ one can employ, we again used the $5 \times 10^{-5}$ molar solution of anthracene dissolved in MTHF. The excitation power $I_{ex}$ was stepwise increased, and the corresponding $OD_T$ values were recorded.

In Figure 2B, we have again plotted $1/I_{ex}$ versus $1/OD_T$ (as circles), with the lowest cw laser power starting at 2 mW and going up to 90 mW. At higher $I_{ex}$ intensities, excessive blooming was observed. At about 40 mW, we observed some increase in the rate of photodecomposition. Because of the rather small triplet-state lifetime $\tau_T$ of anthracene (a fraction of a second), the steady state is quickly reached, allowing one to obtain $OD_T$ values quickly, before photodecomposition becomes effective. Judging from experiments performed in the past, about 100 mW is the highest power $I_{ex}$ one can use, before blooming/melting or excessive photodecomposition starts. From Figure 2B, one may conclude that McClure's method holds up very well to about 100 mW, at least for anthracene. As can be seen from Figure 2B, the
points taken at higher power levels converge quite well into the point \( 1/\text{OD}_T = 0.66 \). At 90 mW, we measure \( \text{OD}_T = 1.48 \), presenting a 97\% conversion ratio. With \( \text{OD}_T = 1.48 \), one would commit only a small error using it instead of \( \text{OD}_T^\infty = 1.52 \).

We did not put error bars on the average \( 1/\text{OD}_T \) values presented in Figure 2A as circles and 2B as crosses. Instead we selected the size of the circles/crosses to be not larger than the largest measurement error. As it can be seen from Table 2, for anthracene, its \( \epsilon_T \) has a measurement error of about \( \pm 3\% \). Each \( 1/\text{OD}_T \) value used to extrapolate for \( 1/\text{OD}_T^\infty \) showed measurement errors of no more than 3\%, often 2\% or less. Small errors are difficult to present accurately by error bars in a graph.

Instead of plotting \( 1/\text{OD}_T \) versus \( 1/I_{\text{ex}} \) to obtain \( 1/\text{OD}_T^\infty \) by extrapolation, we plotted \( \text{OD}_T \) versus \( I_{\text{ex}} \) and present the obtained curve in Figure 3. This Figure illustrates well of how \( \text{OD}_T^\infty \) is approached with increasing excitation power \( I_{\text{ex}} \). Even if one could double the excitation power \( I_{\text{ex}} \) to 200 mW, the conversion to triplet state molecules \( N_T \) would be only about 99\%.

In summary (and in something of a generalization), one could have obtained rather accurate \( \epsilon_T \) values of the compounds we studied without using McClure's method. High conversion ratios were obtained with rather low excitation powers \( I_{\text{ex}} \), as shown in Table 2. Using higher powers, ranging for example from 10 to 100 mW, and assuming no excessive photodecomposition occurs, conversion ratios of 98 to 99\% should be obtainable for most of the compounds we studied. On the other hand, only very few
organic compounds possess all the necessary photophysical properties such as strong T-T absorption and long triplet-state \( \tau_T \) lifetime, together with good photostability. For the many other organic compounds that do not possess these properties, using McClure's method together with cw laser excitation presents experimentally a very convenient way to obtain rather reliable \( \alpha_T(\lambda) \) values.

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REFERENCES


FIGURE 1

Experimental arrangement. MLS, monitoring light source; L₁-L₄, lenses; PH, pinhole in monochromator dovetail plate; BS, laser beam stop; F₁, filter that absorbs the laser light; LND, liquid nitrogen dewar; S, sample; M, mirror with hole in center; PM, power meter; NDF, neutral density filter; F₂, filter that passes laser light only.
FIGURE 2

Plot of $1/OD_T$ versus $1/I_{ex}$ to obtain $1/OD_T^\infty$ by extrapolation

$1/I_{ex} \rightarrow 0$ for anthracene at the concentration $5 \times 10^{-5}$ molar, dissolved in 2-methyltetrahydrofuran. A: The highest cw laser excitation power $I_{ex}$ was 2 mW (the point 0.5) and the lowest 0.5 mW (the point 2.0). B: Plot of $1/OD_T$ vs $1/I_{ex}$ to obtain $1/OD_T^\infty$ by extrapolation at high excitation powers $I_{ex}$ to test McClure's method. The highest cw laser excitation power was 90 mW and the lowest 2 mW.
FIGURE 3

Plot of triplet optical density $\text{OD}_T$ as function of cw laser excitation intensity (power) $I_{\text{ex}}$ to demonstrate how $\text{OD}_T^{\infty}$ is approached at high $I_{\text{ex}}$ powers. The compound studied was anthracene, dissolved in 2-methyltetrahydrofuran, $5 \times 10^{-5}$ molar concentration.
TABLE 1

Measured triplet extinction coefficients $\varepsilon_T$ (l/mole cm) and their averages of pyrene. Measurements were performed at the maximum of T-T absorption at $\lambda_m = 415$ nm, using two different concentrations $N_S$, and with maximum cw laser power $I_{ex}$ of 10 mW.
TABLE 2

Measured triplet extinction coefficients $\epsilon_T$ (l/mole cm) of organic compounds at the maximum $\lambda_m$ (in nm) of T-T absorption. Each $\epsilon_T$ presented is the average of three separately determined (extrapolated) $\epsilon_T$ values. $\lambda_{cw}$ is the wavelength of the exciting cw laser line(s), $I_{ex}$ is the maximum cw laser power (in mW) employed. $N_T$ (%) is the percentage of the original concentration $N_S$ converted into the triplet state at maximum excitation power $I_{ex}$ used. Concentration $M$ of $N_S$ is in mole/l and glassy solvents employed. E:M ethanol:methanol ratio 3:1 and MTHF 2-methyl-trahydrofuran. $<\epsilon_T>$ in l/mole cm is the tentative standard triplet extinction coefficient listed in Table 5 of ref. 1.
### TABLE 1

<table>
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<th>Concentration of Pyrene</th>
<th>$\epsilon_T (\ell/\text{mole cm})$</th>
<th>$\epsilon_T (\ell/\text{mole cm})$</th>
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<td>29,700</td>
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<td></td>
<td>26,500</td>
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<tr>
<td></td>
<td>27,200</td>
<td>30,200</td>
</tr>
<tr>
<td><strong>Average</strong></td>
<td>$27,200 \pm 1.8%$</td>
<td>$29,900 \pm 0.7%$</td>
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<tr>
<td>$1x10^{-4}$ M</td>
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<td></td>
</tr>
<tr>
<td>Compound</td>
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<td>$\lambda_{cw}$ (nm)</td>
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<tr>
<td>---------------------</td>
<td>------------------</td>
<td>---------------------</td>
</tr>
<tr>
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<td>Pyrene</td>
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<td>351.1/363.8</td>
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<tr>
<td>Pyrenecarboxaldehyde</td>
<td>440</td>
<td>351.1/363.8</td>
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