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Journal of Photochemistry and Photobiology A: Chemistry 149 (2002) 45–54

Journal of Photochemistry and Photobiology A:Chemistry

www.elsevier.com/locate/jphotochem

Search for vibronic spin–orbit interactions in the triplet-manifold of phenanthrene *N*-heterocyclic analogues

Theodore G. Pavlopoulos

US Space and Naval Warfare Systems Center, D361, San Diego, CA 92152-5001, USA

Received 3 May 2001; received in revised form 4 January 2002; accepted 10 January 2002

Abstract

After detecting vibronic spin–orbit interactions in the triplet-manifold of some anthracene heterocyclics, we were interested in detecting the presence of these interactions in phenanthrene *N*-heterocyclics. These interactions appear to reduce triplet–triplet (T–T) intensities (oscillator strength f_T values) in aromatic heterocyclics. This effect is important to laser dye technology. Reducing T–T absorption intensities in laser dyes results in reduced triplet-state losses and therefore, in higher laser-action efficiencies. To obtain more experimental evidence on this effect, the T–T absorption spectra of phenanthrene, 5,6- and 7,8-benzoquinoline, phenanthridine, and 1,7- and 4,7-phenanthroline over the violet/green spectral region were measured. This is the spectral region where the ${}^3A_1{}^- \leftarrow {}^3B_2{}^+$ transition of phenanthrene is located. To obtain these T–T absorption spectra, the steady-state method was employed, using the 337.4 nm line from a cw ion krypton laser for excitation. From the recorded triplet optical densities $OD_T(\lambda)$, the triplet extinction coefficients $\varepsilon_T(\lambda)$ were obtained by McClure's intensity variation method. The triplet oscillator strengths f_T of the ${}^3A_1{}^- \leftarrow {}^3B_2{}^+$ transition of phenanthrene and the corresponding transitions in the *N*-heterocyclics were also obtained by integration. Due to measurement errors, the uncertainty of integration limits needed to obtain the f_T values, and overlap with neighboring transitions, inconclusive results were obtained for 5,6- and 7,8-benzoquinolines and phenanthridine. However, the f_T values for 1,7- and 4,7-phenanthroline were considerably smaller than the f_T value obtained for phenanthrene. This suggests the presence of vibronic spin–orbit interactions in these two compounds. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Triplet–triplet absorption; Vibronic spin–orbit interactions in heterocyclics; Laser dyes

1. Introduction

Albrecht [1] and Lim and Yu [2–4] discussed the possibility that vibronic coupling in the triplet-manifold of heterocyclics could introduce vibrational induced intensities, containing unsymmetrical modes in their phosphorescence spectrum. Performing a vibrational analysis of the phosphorescence spectrum of phenazine, Pavlopoulos [5] found evidence of strong vibronic spin–orbit interactions in this molecule. Fig. 1 [6] depicts possible vibrational coupling schemes (A–C) present in the singlet- and triplet-manifolds of *N*-heteroaromatics.

However, it appears that there is another manifestation of vibrational spin–orbit coupling in the triplet-manifold of heterocyclics—namely, the reduction of T–T absorption intensities. Connecting many experimental observations with molecular structures of laser dyes, Drexhage [7] stated in his loop rule. "In a dye, where the π-electrons of the chromophore can make a loop when oscillating between the end groups, the triplet yield will be higher than in the related compound where the loop is blocked." Or, somewhat rephrased: in a dye, triplet-state losses (triplet yields) will be lower when the chromophore contains heteroatom(s), as compared to the related dye, where the chromophore does not contain heteroatom(s). Triplet-state losses (TSLs) are the main loss mechanism present in laser dyes. Lowering these losses implies higher laser-action efficiencies.

During excitation, transient triplet-state dye molecules of concentration N_T are produced. These molecules will absorb laser light, depending on their triplet extinction coefficient $\varepsilon_T(\lambda_L)$ at the laser-action frequency λ_L and N_T. The λ_L covers most of the fluorescence spectral region λ_F of the laser dye. Therefore, TSLs are given by

$$\mathrm{TSL} = N_T \varepsilon_T(\lambda_F) \qquad (1)$$

Trying to explain Drexhage's loop rule, Pavlopoulos [8] came to the following conclusion. Measuring quantum fluorescence, Q_F values of efficient laser dyes, it is known that their Q_F values are high ($Q_F \approx 1$). This implies that all N_T values in laser dyes, during excitation, must be small. Therefore, according to Eq. (1), one is forced to conclude that $\varepsilon_T(\lambda)$ values in laser dye chromophores that contain

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E-mail address: pavlopou@spawar.navy.mil (T.G. Pavlopoulos).

PII: S1010-6030(02)00018-7

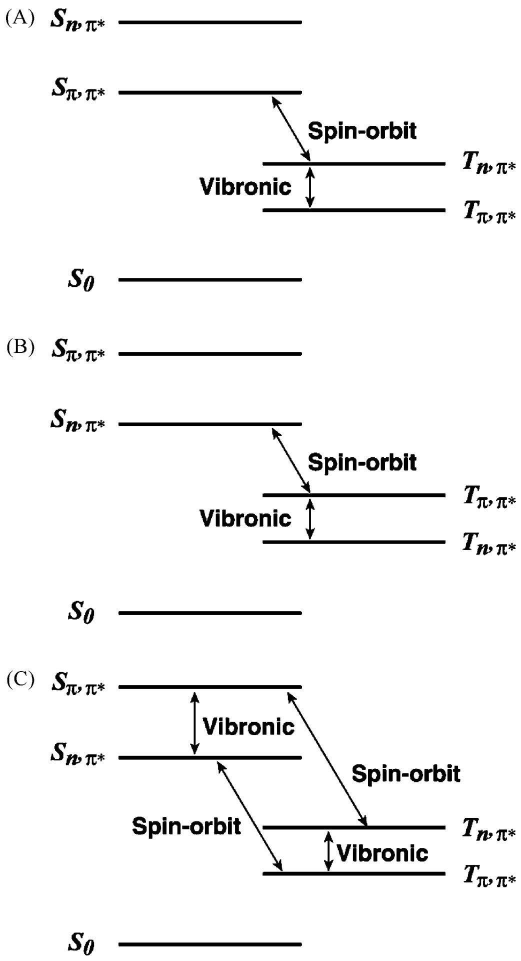

Fig. 1. Vibrational coupling schemes (A–C) possibly present in the singlet- and triplet-manifolds of *N*-heteroaromatics.

heteroatom(s) must be smaller relative to the corresponding value in laser dyes where the parent chromophores does not contain heteroatom(s).

This observation can be explained by the presence of strong vibronic spin–orbit coupling (mixing) between the triplet (n, π^*) and triplet (π, π^*) states in heterocyclics. The (n, π^*) absorption reduces (steals) intensity from the triplet (π, π^*) absorption and, of course, increases (n, π^*) absorption intensities present in different regions of the spectrum. Reduced triplet (π, π^*) absorption intensities results in reduced TSL, and therefore, in increased laser-action efficiencies.

To test this observation experimentally, one has to compare f_T values present in chromophores with the corresponding f_T values present in their heterocyclic analogues.

Therefore, the triplet oscillator strength f_T of anthracene's T–T band located in the violet/blue portion of the spectrum (the $^3B_b \leftarrow {}^3L_a$ transition) was recorded ($f_T = 0.29$) and compared with the f_T values of some of its heterocyclic analogues. The obtained f_T value for anthracene was considerably larger when compared with the corresponding values for acridine, $f_T = 0.12$, and phenazine, $f_T = 0.13$ [8]. This rather strong reduction of triplet (π, π^*) transition intensities in the two anthracene heterocyclics strongly supports the earlier suggestion that vibronic spin–orbit interactions between their triplet (n, π^*) and (π, π^*) states reduces T–T absorption.

Because of the general interest of this effect, additional heterocyclic systems should be studied. Here, we report the f_T values of phenanthrene and some of its *N*-heterocyclics analogues. Also, theoretical calculations of the magnitude of this effect would be desirable.

2. Spectroscopy of heterocyclics

Substituting a carbon atom with a heteroatom (e.g. nitrogen) in an aromatic ring introduces (n, π^*) transitions. This reduces the symmetry of the molecule. However, such a substitution does not generally affect the overall appearance of the near UV–VIS absorption spectrum of the heterocyclics. Following heteroatom substitution, some absorption bands may experience small wavelength shifts, slight increases or decreases in intensity, or some vibrational structure may appear or disappear. The newly introduced (n, π^*) transitions are often not observed because they are weak (generally, in the 100 L/(M cm) range). They are often submerged under the stronger (π, π^*) bands.

However, heteroatom substitution profoundly affects the luminescence (fluorescence and phosphorescence) properties of heterocyclics. If the (n, π^*) transitions are of lowest energy, none or only weak fluorescence is observed. Most often, one observes strong phosphorescence intensities. However, if the (π, π^*) transitions are of lowest energy, strong fluorescence may be observed. More details on (n, π^*) transitions can be found, in review articles by Sidman [9], Kasha [10], Kummer and Zimmermann [11], and Mason [12,13].

3. Materials and methods

3.1. Chemicals and solvents used

Phenanthrene (99.999%) was obtained from Hinton. 5,6-Benzoquinoline was purchased from K&K Laboratories. This compound was re-crystallized, using an ethanol/water mixture as solvent. 7,8-Benzoquinoline was obtained from Chemical Procurement Laboratories and was also re-crystallized, using cyclohexane as solvent. Phenanthridine (98%) and 4,7-phenanthroline (98%) were used without purification. These two compounds, together with 2-methyltetrahydrofuran were obtained from Aldrich.

3.2. Triplet–triplet absorption spectra of organic compounds

Experimentally, it is difficult to obtain accurate $\varepsilon_T(\lambda)$ values. Therefore, there is a shortage of experimental data on the $\varepsilon_T(\lambda)$ values of organic compounds, especially on heteroaromatics. Carmichael and Hug [14] in their review article on T–T absorption spectra of organic compounds, listed data on only 1143 compounds, of which less than half report $\varepsilon_T(\lambda)$ values. A large percentage of these values listed in [14] are of limited accuracy. Several of the $\varepsilon_T(\lambda)$ values reported in the literature were obtained by flash photolysis, employing the depletion method. However, measuring $\varepsilon_T(\lambda)$ values accurately under pulsed excitation is difficult.

Details of the methods for obtaining $\varepsilon_T(\lambda)$ values of organic compounds, and also discussion on the measurement accuracy is provided in [14]. For our experiments, we employed the convenient intensity variation method proposed by McClure [15].

A convenient way to obtain T–T absorption spectra of many organic compounds is to use the steady-state excitation method, together with cw laser excitation. This method is experimentally simple and provides fairly accurate $OD_T(\lambda)$ and $\varepsilon_T(\lambda)$ values. The experimental setup of this method has been described in detail in [16–19].

By focusing the cw laser beam on the sample with the aid of the lens, high concentrations N_T of triplet-state molecules are generated in a very small volume. This tiny excitation area is focused with the aid of another lens on a small hole in the dovetail plate, covering the monochromator slit. A monitoring white light beam from the point source is also passing through the small excitation area. It is experiencing strong attenuation from the high concentration N_T of triplet-state molecules present. The monitoring light beam intensities are recorded on a strip-chart recorder, thus, providing a convenient way to obtain triplet optical densities $OD_T(\lambda)$ values.

Triplet optical density $OD_T(\lambda)$, similar to other optical densities, are defined by

$$OD_T(\lambda) \equiv \log \frac{I_T}{I_0} = N_T \varepsilon_T(\lambda) d, \tag{2}$$

where I_0 is the intensity of the monitoring light with the cw laser excitation off and I_T is the intensity with the cw laser excitation on, d is the thickness of the sample.

3.3. Obtaining triplet extinction coefficients

The $\varepsilon_T(\lambda)$ values are obtained by using McClure's intensity variation method [15,18–22]. One varies the excitation intensity (power) I_{ex} of the excitation cw laser light and records the corresponding $OD_T(\lambda)$ values:

$$\frac{1}{OD_T(\lambda)} = \frac{1}{N_T \varepsilon_T(\lambda) d}\left(1 + \frac{A_i}{I_{ex}}\right), \tag{3}$$

where A_i contains all the rate constants effective in the singlet- and triplet-manifolds.

The following procedure is used to obtain $\varepsilon_T(\lambda)$ values from McClure's equation (Eq. (3)). First, the T–T absorption spectrum of the compound is obtained by recording $OD_T(\lambda)$ values. Second, at a spectral region of strong T–T absorption, e.g. at a T–T absorption maximum λ_M, one varies the cw laser excitation intensities I_{ex} and records the resulting $OD_T(\lambda_M)$ values.

Four $I_{ex}(1), \ldots, I_{ex}$ were selected in such a way that $1/I_{ex}(1), \ldots, 1/I_{ex}$ were equidistant from each other. This yielded four $1/OD_T(1), \ldots, 1/OD_T(4)$ values. Three to four such measurements were obtained, yielding three to four sets of $1/OD_T(1), \ldots, 1/OD_T(4)$ values. From the three to four sets of measurements obtained, the average values $1/OD_T(1), \ldots, 1/OD_T(4)$ were formed and used to extrapolate the $1/OD_T(\lambda_M)^\infty$ value. The $\varepsilon_T(\lambda_M)$ value was obtained with the aid of Eq. (4).

A plot of the different $1/OD_T(\lambda_M)$ values against the $1/I_{ex}$ values, according to Eq. (3), yields a straight line. The intersections of this straight line with the ordinate, i.e. $1/I_{ex} \to 0$ or $I_{ex} \to \infty$ yields $1/OD_T(\lambda_M)^\infty$. If one could use $I_{ex} = \infty$ excitation power, all singlet ground-state molecules of concentration N_S would have been converted into triplet-state molecules of concentration N_T, i.e. $N_S = N_T$:

$$\frac{1}{OD_T(\lambda_M)^\infty} = \frac{1}{N_S \varepsilon_T(\lambda_M) d}, \quad \text{or}$$
$$OD_T(\lambda_M)^\infty = N_S \varepsilon_T(\lambda_M) d, \tag{4}$$

where $\varepsilon_T(\lambda_M)$ can be obtained from Eq. (4) because $OD_T(\lambda_M)^\infty$ has been extrapolated, and d is known. We measured at least two such $\varepsilon_T(\lambda_M)$ values, each taken at a different concentration to guard saturation at low temperatures [18–22]. However, saturation was not a problem for this study because all the compounds we studied were very soluble in 2-methyltetrahydrofuran. Because the experiments were performed at liquid nitrogen temperatures, the concentration N_S had to be corrected for volume contraction. The contraction factor $\rho = 0.84$ was used for 2-methyltetrahydrofuran [20].

For excitation, a Model 2025-11 Spectra-Physics cw ion krypton laser, was used. Excitation powers (intensities I_{ex}) were measured with a Liconix Model 45PM-meter.

3.4. Obtaining oscillator strength values

Absorption bands of organic compounds may change their spectral location with the change of solvent. Also, the width, vibrational structure, and spectral location of an absorption band may be affected by the change of solvent. Therefore, a proper measure of the strength of a transition is not the maximum intensity (extinction coefficient), but its oscillator strength f. To obtain this f value, the $\varepsilon(\lambda)$ values of the absorption band are first obtained. Then, these values are converted to $\varepsilon(\nu)$ values, with ν expressed in wave numbers (cm^{-1}). The oscillator strength f is obtained by integration over the entire absorption band, stretching from a to b [23]:

$$f = 4.33 \times 10^{-9} \int_a^b \varepsilon(\nu)\, d\nu. \tag{5}$$

3.5. Estimation of experimental errors

To derive meaningful spectroscopic information from the obtained triplet f_T values, a discussion on the accuracy of these values is necessary. Unfortunately, the magnitude of some of these errors is difficult to estimate. Some of the errors present in the $\varepsilon_T(\lambda)$ values have been discussed in [21,22]. The experimental $\varepsilon_T(\lambda)$ values, we later present should be accurate within ±5–10%. In the following sections, we review the four most important sources of measurement errors.

3.5.1. Photodecomposition

To some degree, photodecomposition is always present when exposing organic compounds to intense radiation. After terminating irradiation and $N_T \approx 0$, one measures $I_0 > I'_0$ due to the presence of absorption by photoproducts. The compounds we studied exhibited only small photodecomposition rates, with I_0/I'_0 in the range of 101–102%. The contribution of the error log I_0/I'_0 is very small to overall measurement accuracy of log I_0/I_T. In our case, small photodecomposition rates in part are due to the small cw laser power I_{ex} needed for excitation.

To reduce measurement errors resulting from photodecomposition products, one has to avoid excitation into an area containing these products. This was accomplished by moving (up or down and left or right) the liquid nitrogen Dewar (and the sample) slightly, to generate an unexposed area on the sample. However, moving the Dewar too frequently may cause a misalignment of the small excitation area that is focused exactly on the small hole in the dovetail blade of the monochromator. This is also a source of measurement error. Performing realignments often can reduce this error.

3.5.2. Bubbles and schlieren

Schlieren are the result of heat gradients present in the liquid nitrogen. Large heat gradients are a source of bubbles. Schlieren and bubbles can be reduced considerably by bubbling gaseous helium above the sample through the liquid nitrogen. The fluctuation of the monitoring light intensities I_0 and I_T caused by in-homogeneities in the liquid nitrogen are in the ±1% range.

3.5.3. Accumulation of small measurement errors

Small measurement errors may add up to large errors. Among small errors present are the concentration $N_S(RT)$ of the solution, obtaining the contraction factor ρ, and the measured thickness of the sample d. These errors should be in the range of ±2%.

3.5.4. Overlap of transitions

If there is only a little overlap with neighboring transitions, i.e. the limits of integration can be identified, no significant measurement errors are introduced in f_T values. Unfortunately, there is often overlap with neighboring transitions present. In some cases, the neighboring transitions were close and broad, making it a guessing game on how to derive their intensity contribution.

Such was the case in this study, making it sometimes difficult, or in some cases impossible, to identify the proper integration limits of the T–T absorption spectra we studied. This contributed to the uncertainty of the f_T values we obtained.

4. Experimental results

4.1. Phenanthrene

The near S–S UV absorption spectrum of phenanthrene exhibits three transitions [24]. From about 350 to 290 nm is stretches a weak absorption band, showing some vibrational structure, the extinction coefficient ε_S is in the range of only 200 L/(M cm). This band presents the $^1L_b \rightarrow {}^1A$ transition, which is short-axis polarized. The stronger $^1L_a \rightarrow {}^1A$ transition is located at approximately 295 nm and is long-axis polarized. At about 250 nm, the strong ^1B_a and ^1B_b transitions overlap [25,26].

Notwithstanding the weakness of the $^1L_b \rightarrow {}^1A$ transition, the T–T absorption spectrum of phenanthrene is one of the most widely studied [14]. Large $OD_T(\lambda)$ values are obtained from flashlamp excitation. Even steady-state excitation into the weak L_b transition with the 312.6/313.2 nm lines from a high-pressure mercury lamp, yields large $OD_T(\lambda)$ values. These large values are due to the long triplet-state lifetime $\tau_T = 3$ s at liquid nitrogen temperatures, together with the rather large $\varepsilon_T(\lambda)$ values of the transitions present in this compound. Rather large $OD_T(\lambda)$ values are obtained, even though the 337.4 nm line from the cw ion krypton laser is poorly absorbed. Only, 1–2 mW of cw laser light was used for excitation. This is also the case for the *N*-heterocyclics we studied. Using these low excitation powers resulted in low photodecomposition rates for all the compounds we studied.

Phenanthrene exhibits a rather strong T–T absorption band, stretching from approximately $a = 400$ nm to $b = 525$ nm, the $^3A_1{}^- \leftarrow {}^3B_2{}^+$ transition [14,27–33]. This is the transition we studied. Later, we refer to the corresponding transition in the *N*-heterocyclics we studied as the "main" transition. The T–T absorption spectrum of phenanthrene is pictured in Fig. 2. Starting from approximately 425 nm to shorter wavelengths, the $^3B_2{}^- \leftarrow {}^3B_2{}^+$ transition appears to be located [27]. Using the 312.6/313.2 nm lines from a mercury high-pressure lamp for excitation a change of the polarization curve P was observed at approximately 425 nm, only slightly overlapping the $^3A_1{}^- \leftarrow {}^3B_2{}^+$ transition [27]. The onset of this transition at 400 nm is marked in Fig. 2.

From 850 nm to shorter wavelengths, the onset of the $^3A_1{}^- \leftarrow {}^3B_2{}^+$ transition at 525 nm, stretches a weak T–T absorption band. It is probably representative of a forbidden transition [14,27–31]. This band possesses the same (positive) polarization as the $^3A_1{}^- \leftarrow {}^3B_2{}^+$ transition [28].

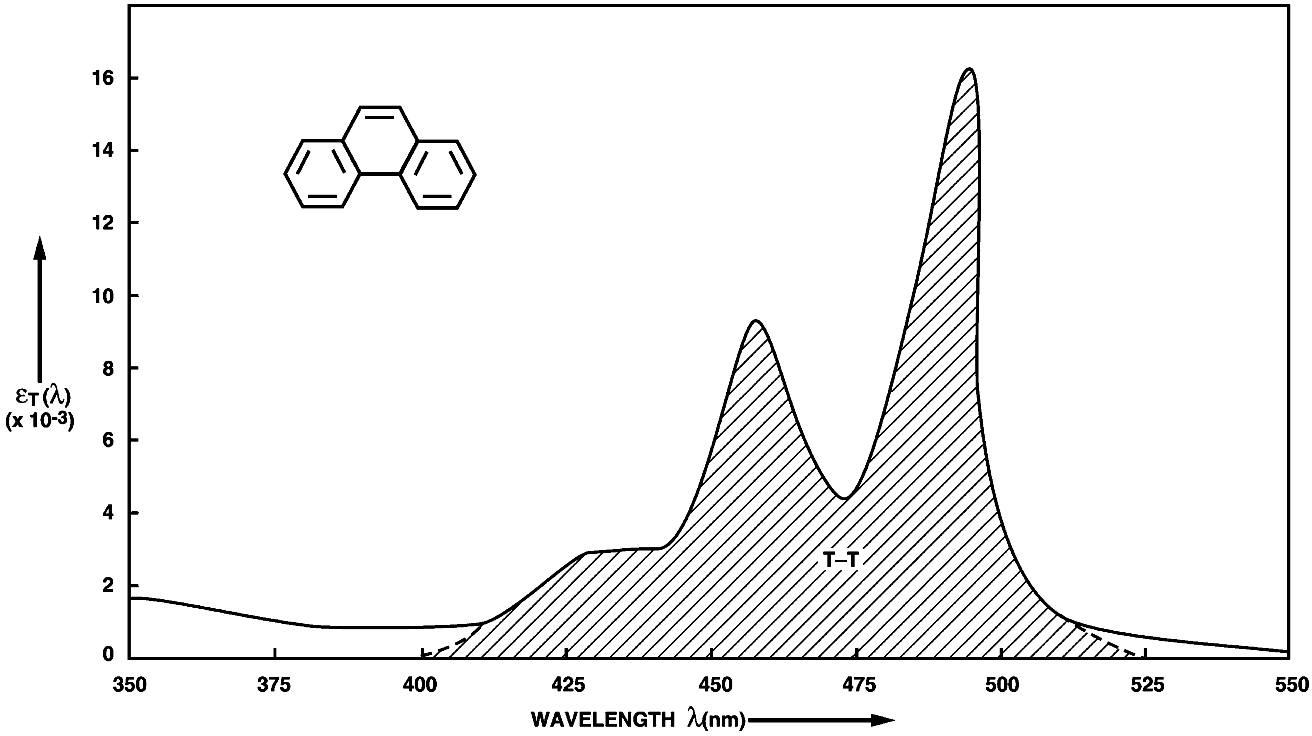

Fig. 2. Triplet–triplet absorption spectrum of phenanthrene.

These two transitions overlap only slightly, and we have marked b as the end of the $^3A_1{}^- \leftarrow {}^3B_2{}^+$ transition at 525 nm. To obtain the f_T value of this transition, integration is performed between 400 and 525 nm, the shaded area.

In Fig. 2, we assume the forbidden transition to stretch only to approximately 510 nm. Even if this transition stretches farther into the spectral region of the $^3A_1{}^- \leftarrow {}^3B_2{}^+$ transition, the resulting error for the f_T should be small. It is assumed that the shaded area depicts the main T–T absorption band (transition). However, as we will see later, this forbidden transition seems to gain in intensity in most of the monoaza heterocyclics we studied, contributing to measurement errors in the reported f_T values.

The 337.4 nm line from the cw ion krypton laser used for excitation is not suitable for polarization studies. It produces a weakly, positively polarized T–T absorption spectrum, and therefore, it could not be used to assist in pinpointing the beginning and end of the two T–T transitions. Therefore, somewhat arbitrarily, we also use the integration limits of $a = 400$ nm and $b = 525$ nm for most of the other *N*-heterocyclics we studied.

The following $\varepsilon_T(\lambda_M)$ values were obtained. A 1.07×10^{-4} M solution yielded a $\varepsilon_T(492) = 16.5 \times 10^3$ and 15.5×10^3 L/(M cm). A 1.86×10^{-4} M solution yielded a $\varepsilon_T(492) = 16.6 \times 10^3$ and 15.5×10^3 L/(M cm). A 2.13×10^{-4} M solution yielded $\varepsilon_T(492) = 16.0 \times 10^3$ and $\varepsilon_T(492) = 16.5 \times 10^3$ L/(M cm). The average of all these $\varepsilon_T(492)$ values is 16.2×10^3 L/(M cm) and is used to obtain the T–T absorption spectrum depicted in Fig. 2.

Converting the $\varepsilon_T(\lambda)$ values to $\varepsilon_T(\nu)$ values and integrating over the shaded region between 400 and 525 nm as indicated in Fig. 2, one obtains a $f_T = 0.11_1$ for the $^3A_1{}^- \leftarrow {}^3B_2{}^+$ transition.

Keller and Hadley report $f_T = 0.11$ [30], and an average value of $f_T = 0.15$ was compiled from different literature data by Lavalette et al. [31]. For later reference, we note that in Fig. 2, we have $\varepsilon_T(400) \approx 1.0 \times 10^3$ L/(M cm) and $\varepsilon_T(525) \approx 1.0 \times 10^3$ L/(M cm).

4.2. 5,6-Benzoquinoline

The near UV absorption spectrum of 5,6- and 7,8-benzoquinoline and phenanthridine are similar to that of phenanthrene [25]. In these compounds, only the lowest energy S–S band experiences a small blue shift and intensification. Craig and Ross [32], West et al. [33], Henry and Lawler [34], and Petrov et al. [35] recorded the T–T absorption spectrum of this compound. Its triplet-state lifetime τ_T is somewhat shorter than that of phenanthrene [14].

A 1.05×10^{-4} M solution yielded $\varepsilon_T(510) = 6.71 \times 10^3$ and 6.52×10^3 L/(M cm), and a 2.09×10^{-4} M solution yielded $\varepsilon_T(510) = 6.38 \times 10^3$ and 6.49×10^3 L/(M cm). Using the average of these four values, we obtained the T–T absorption spectrum depicted in Fig. 3. Integrating over the shaded area between 400 and 535 nm, we obtained $f_T = 0.09_5$ for the main band. According to Fig. 3, we have $\varepsilon_T(400) \approx 2.3 \times 10^3$ L/(M cm) and $\varepsilon_T(550) \approx 1.2 \times 10^3$ L/(M cm). Both transitions have experienced an intensity

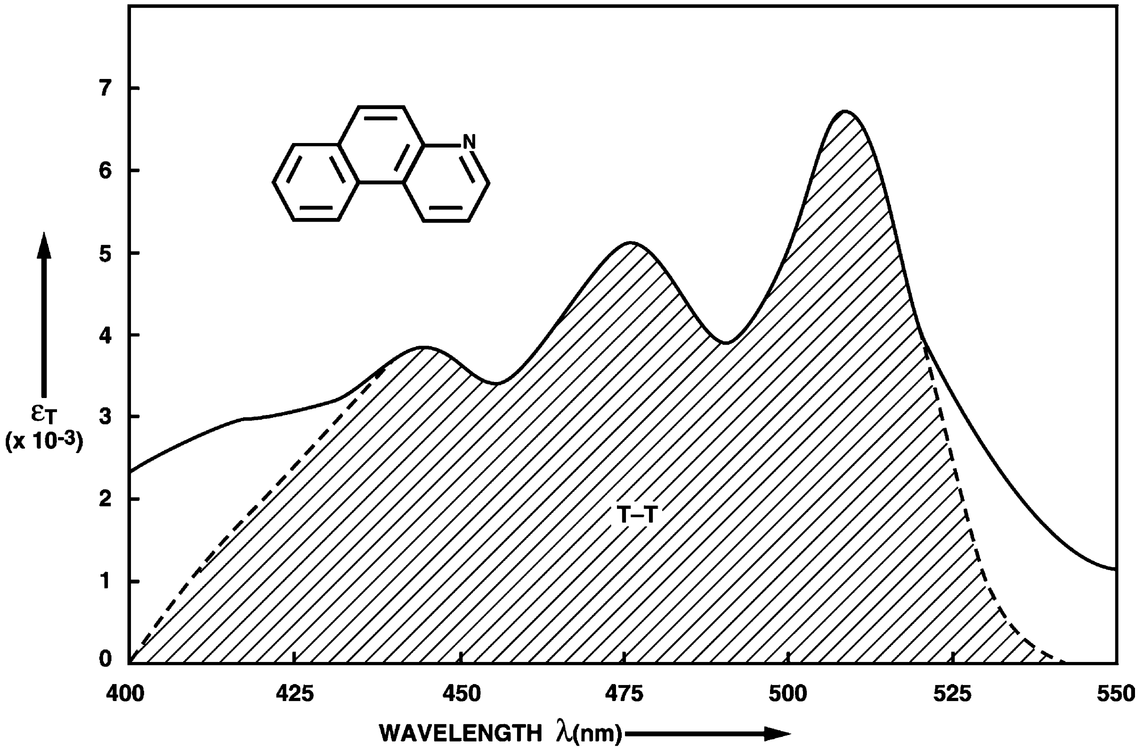

Fig. 3. Triplet–triplet absorption spectrum of 5,6-benzoquinoline.

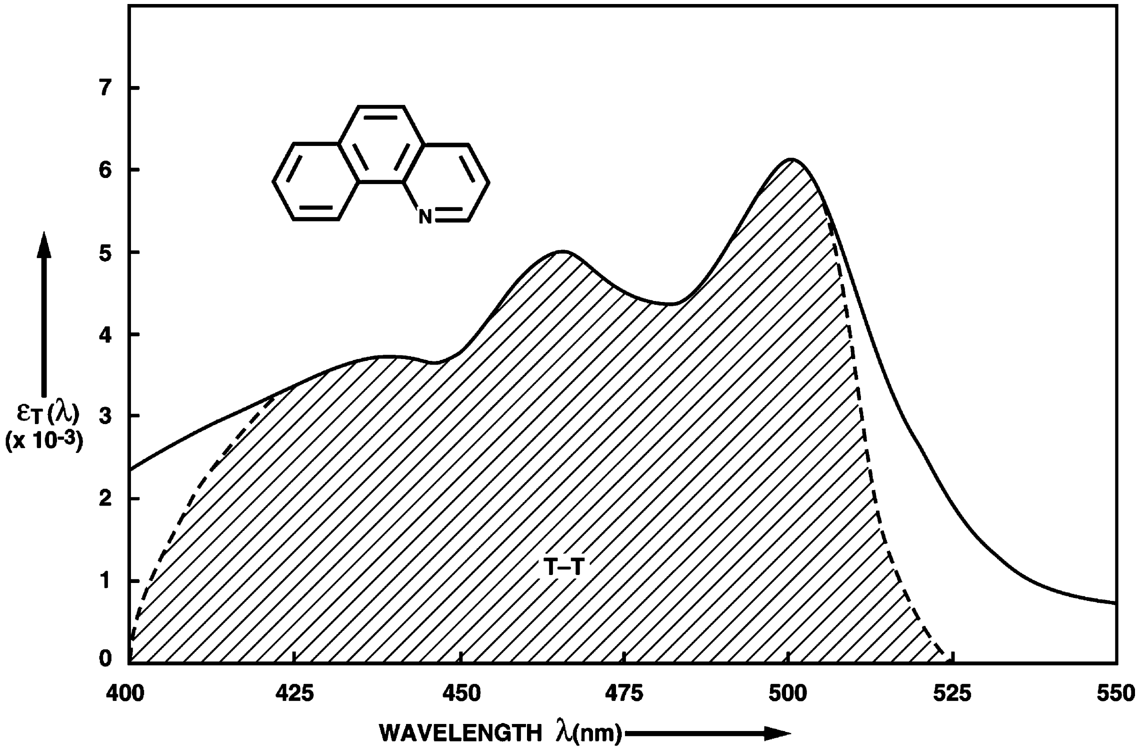

Fig. 4. Triplet–triplet absorption of 7,8-benzoquinoline.

increase of about 100%, following *N*-heteroatom substitution. The intensity probably increased because of reduction in molecular symmetry [36].

4.3. 7,8-Benzoquinoline

Craig and Ross [32], West et al. [33], Henry and Lawler [34], and Petrov et al. [35] recorded the T–T absorption of this compound.

A 1.15×10^{-4} M solution yielded $\varepsilon_T(500) = 6.02 \times 10^3$ L/(M cm) and a 2.30×10^{-4} M solution yielded $\varepsilon_T(500) = 6.45 \times 10^3$ L/(M cm). Again, the average of these two values is used, and the T–T absorption of this compound is presented in Fig. 4. Because the T–T absorption maximum of this compound is located at 510 nm, we integrated over the shaded area from 400 to 525 nm and obtained $f_T = 0.09_1$ for the main band. According to Fig. 4, $\varepsilon_T(400) \approx 2.4 \times 10^3$ L/(M cm), which is an approximately 100% intensity increase, and $\varepsilon_T(550) \approx 0.8 \times 10^3$ L/(M cm).

4.4. Phenanthridine

West et al. [33] and Petrov et al. [35] also obtained the T–T absorption spectrum of this compound.

When a 1.01×10^3 M solution, we recorded $\varepsilon_T(525) = 3.45 \times 10^3$ L/(M cm), and when using a 2.01×10^3 M solution, we recorded $\varepsilon_T(525) = 3.61 \times 10^3$ L/(M cm). The T–T absorption spectrum from 400 to 600 nm of this compound is presented in Fig. 5. This T–T absorption spectrum does not resemble that of phenanthrene. Both the ${}^3B_2{}^- \leftarrow {}^3B_2{}^+$ transition at the short-wavelengths' side of the ${}^3A_1{}^- \leftarrow {}^3B_2{}^+$ transition (the main band), as well as the forbidden transition to its long wavelength side has gained considerable in intensity. Consequently, strong overlapping of these transitions is present. Integration over the shaded area and with the integration limits of $a = 400$ nm and $b = 525$ nm, yields $f_T = 0.08_2$ for the main band. According to Fig. 5, $\varepsilon_T(400) \approx 3.0 \times 10^3$ L/(M cm), presenting an intensity gain of about 300%. $\varepsilon_T(525) \approx 3.8 \times 10^3$ L/(M cm) presents a gain of approximately 600%. Due to the strong overlapping with neighboring T–T transitions, the obtained f_T value is burdened with considerable errors.

4.5. 1,7-Phenanthroline

This compound, together with 4,7- and 1,10-phenanthroline exhibits near-UV absorption spectra, which are similar to that of phenanthrene [25]. However, the lowest energy weak absorption spectrum is blue-shifted. Also, its intensity, contrary to the monoaza derivatives, is reduced. Consequently, the 337.7 nm line was even more weakly absorbed, compared to the four previously studied compounds. Therefore, higher concentrations had to be used.

The T–T absorption spectrum of this compound was also recorded by Petrov et al. [35].

A 2.70×10^{-4} M solution yielded $\varepsilon_T(470) = 2.49 \times 10^3$ L/(M cm), and a 5.71×10^{-4} M solution yielded $\varepsilon_T(470) = 2.50 \times 10^3$ L/(M cm). Using the averages of these two values, the T–T absorption spectrum of this compound is depicted in Fig. 6. Integrating over the shaded area and using the limits shown in the Fig. 6, we obtained a $f_T = 0.07_0$ for the main transition. This is about

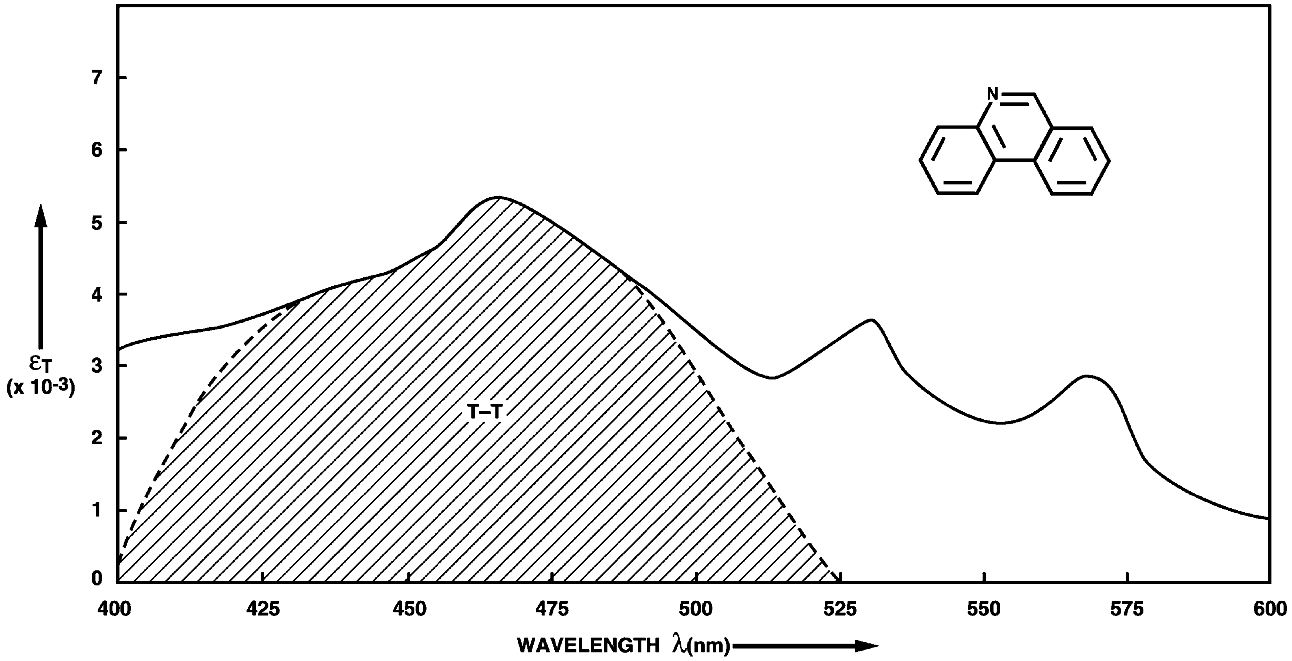

Fig. 5. Triplet–triplet absorption spectrum of phenanthridine.

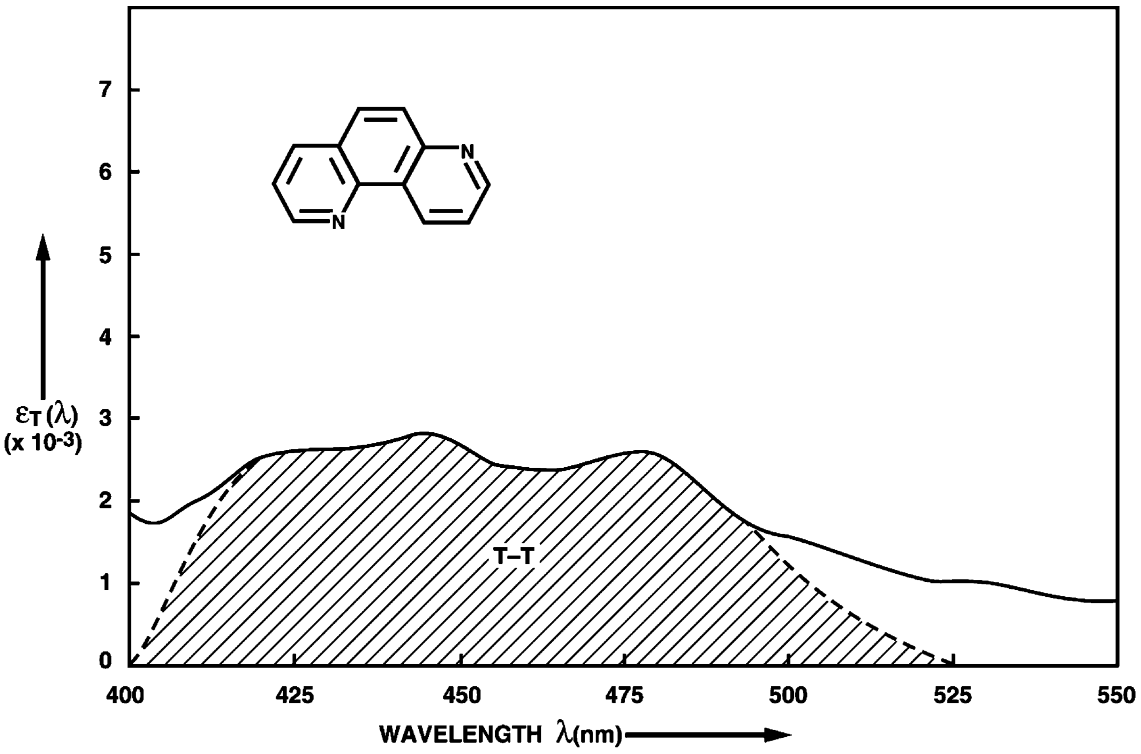

Fig. 6. Triplet–triplet absorption spectrum of 1,7-phenanthroline.

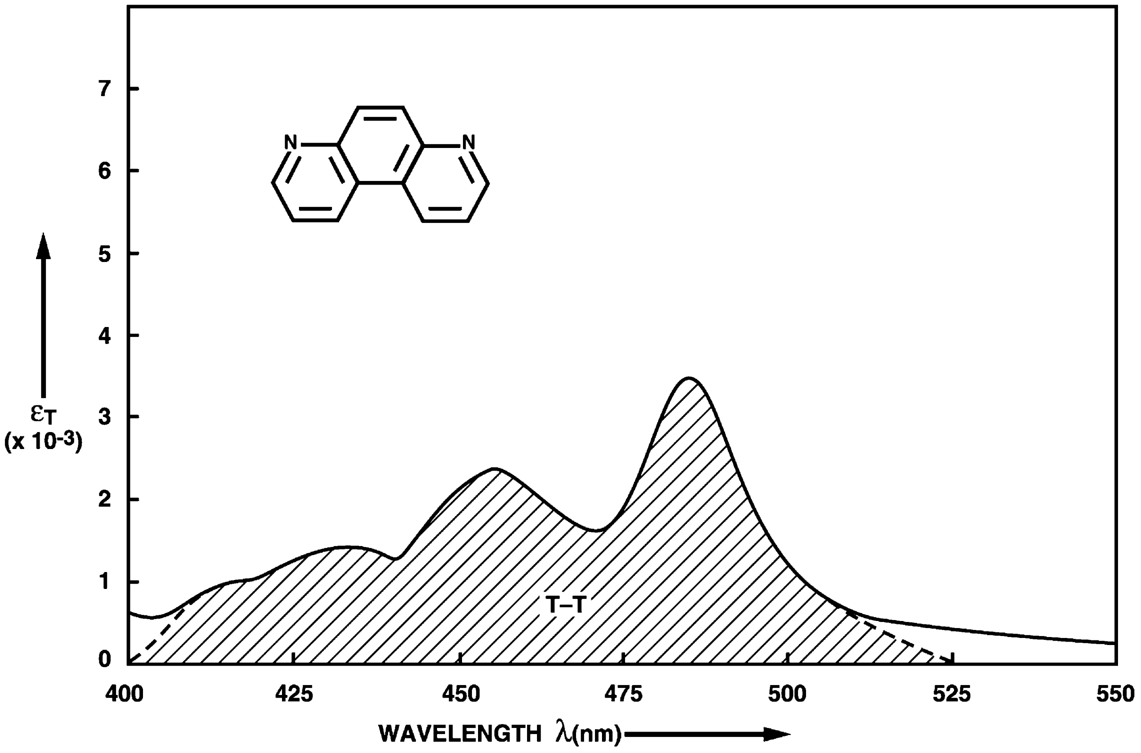

Fig. 7. Triplet–triplet absorption spectrum of 4,7-phenanthroline.

one-half of the value obtained for phenanthrene, suggesting the presence of vibronic spin–orbit interactions. According to Fig. 6, $\varepsilon_T(400) \approx 1.8 \times 10^3$ L/(M cm) and $\varepsilon_T(525) \approx 1.0 \times 10^3$ L/(M cm).

4.6. 4,7-Phenanthroline

The T–T absorption spectrum of this compound has also been recorded by Petrov et al. [35]. The spectrum we obtained is depicted in Fig. 7. The slight dip at about 405 nm may indicate the onset of the neighboring transition, the ${}^3B_2{}^- \leftarrow {}^3B_2{}^+$ transition in phenanthrene.

The 2.10×10^3 M solution yielded $\varepsilon_T(485) = 3.44 \times 10^3$ L/(M cm), and the 4.20×10^3 M solution, $\varepsilon_T(485) = 3.45 \times 10^3$ L/(M cm). According to Fig. 7, $\varepsilon_T(400) \approx 0.7 \times 10^3$ L/(M cm) and $\varepsilon_T(525) \approx 0.4 \times 10^3$ L/(M cm). With these small values, as in phenanthrene, there should be only minimal overlapping in these two spectral regions.

Integrating between 400 and 535 nm, one obtains $f_T = 0.03_6$ for this band. This value is about three times smaller than the value obtained for phenanthrene. Also here, there seemed to be strong vibronic spin–orbit interactions present.

4.7. 1,10-Phenanthroline

For this compound, even at higher concentrations, only weak T–T absorption was obtained. This made it difficult to obtain accurate $\varepsilon_T(\lambda)$ values, and therefore, no data are reported.

5. Summary and discussion of experimental results

We emphasized that the S–S absorption spectra of aromatic *N*-heterocyclics, in general, resemble their parent aromatic hydrocarbon S–S absorption spectrum. Although most of the T–T absorption spectra of the heterocyclics we studied were similar to phenanthrene, this was not the case for phenanthridine and 1,7-phenanthroline.

For the monoaza derivatives we studied, we observed a considerable increase in the intensity of both the transitions located on the short as well as on the longer wavelength side of the main T–T absorption band. These increased intensities probably extended considerably into the spectral region of the main transition, resulting in inaccurate f_T values. Even if we assume that the integration limits we used for the main transition were proper, we were not able to correct (derive) accurately the intensity contributions of the neighboring two T–T absorption bands.

Nevertheless, the f_T values for the main transition we obtained for the monoaza heterocyclics, were all somewhat lower than the f_T value of phenanthrene. If we had been able to estimate the intensity contributions of the two overlapping bands, the resulting f_T values for the main bands might have been even smaller. This is especially true for phenanthridine. In short, the monoaza heterocyclics of phenanthrene are not the best candidates for detecting a reduction of triplet (π, π^*) transition intensities due to the presence of vibronic spin–orbit interactions.

However, in 1,7-phenanthroline, the $\varepsilon_T(400)$ and $\varepsilon_T(525)$ values present are small and even smaller in 4,7-phenanthroline. The obtained experimental results do support the suggestion that vibronic spin–orbit interactions are present in these two *N*-heterocyclics, causing considerable reduction of the intensity of the main triplet (π, π^*) absorption band.

Heterocyclic atom(s) substitution into aromatic molecules reduces the intensity of some of their T–T absorption bands. In laser dyes, reducing $\varepsilon_T(\lambda_F)$ values reduces TSL. This implies that efficient laser dyes may be found among compounds that besides possessing high Q_F values ($Q_F \approx 1$) contain only five-and six-membered heterocyclics [37].

Acknowledgements

The author wishes to thank Mr. W.A. Friday, US Army AMCOM, who provided partial funding for this research.

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