

Thermodynamic energies of donor and acceptor triplet states

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Abstract

Thermodynamic energies (E_T) of lowest triplet states (T_1) have been measured for 60 triplet energy donors and acceptors. Laser flash photolysis procedures were used to monitor the equilibration between the triplet–triplet absorptions of reference and unknown compounds in ethyl acetate at 295 K. These measurements provide triplet free energies that reflect both enthalpy and entropy differences between T_1 and the ground state (S_0). These thermodynamic energies are the basis of quantitative models for triplet energy transfer kinetics in solution. For comparison, T_1 energies were also measured via phosphorescence at 295 K for most of the donors and many of the acceptors of this study. The phosphorescence of naphthalene at 295 K served as a reference for relating the thermodynamic and phosphorescent triplet energies (E_P). For most rigid molecules the E_T and E_P values are nearly identical. However, for molecules with considerable rotational or conformational freedom, such as ketocoumarin and α -diketone donors and polyphenyl acceptors, E_T values tend to be substantially greater than E_P values. This difference partially reflects the tendency for reduced rotational freedom in T_1 relative to S_0 , which leads to a reduction in entropy and a corresponding increase in free energy (from $-T\Delta S$) in T_1 . For nonrigid chromophores triplet energies obtained from low-temperature measurements tend to approximate E_T values in some cases, because the energy increases associated with emission from unrelaxed triplets tend to parallel the positive contributions of decreased T_1 entropy to E_T . Triplet–triplet absorption maxima and extinction coefficients are provided for all of the donors and acceptors. Intersystem crossing quantum yields, also measured by laser flash photolysis, are provided for the triplet energy donors.

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1. Introduction

Due to their relatively long lifetimes, the lowest triplet states (T_1) of organic molecules play a prominent role in many photochemical and photobiological processes. It is critical to the understanding of such processes that the energies of T_1 be accurately determined. Most theoretical treatments of triplet energy transfer kinetics also relate quantitatively to the T_1 energies of donor and acceptor molecules [1–4].

It has been customary to use T_1 energies obtained from low-temperature (e.g., 77 K) phosphorescence spectra for prediction and analysis of triplet energy transfer. However, these energies

may be inappropriate for several reasons. First, the rigid low-temperature matrix may inhibit nuclear relaxation in the triplet state of the emitter relative to the extent of relaxation that occurs in a low-viscosity solution. This may result in higher apparent T_1 energies in the former situation. Substantial density increases can occur at 77 K (e.g., $\sim 20\%$ for ethyl acetate), which increase solvent polarizability and can significantly alter triplet energies. Inhibited reorientation of solvent dipoles at low temperatures may also alter triplet energies. For some molecules the lack of entropy information represents the largest source of uncertainty that may arise from use of low-temperature phosphorescence energies. Entropy differences between the T_1 and S_0 can be considerable for molecules with rotational or conformational freedom. For example, $-T\Delta S$ values at 295 K of approximately 0.5–2 kcal/mol have been determined for benzophenone and biphenyl derivatives [5–7].

Equilibration between triplet states depends on free energy differences rather than simple enthalpy differences according to $\Delta G = -RT \ln K$. Theories for the kinetics of triplet energy

Abbreviations: BP, benzophenone; 2MeOTX, 2-MeO thioxanthone (2-methoxythioxanthone); DEB, 2,2'-diethoxybenzil; BDEAC, bis DiEtAm coum (3,3'-carbonylbis(7-diethylaminocoumarin)); IMP, 1-Me phenanthrene (1-methylphenanthrene); NAP, naphthalene; 4BTP, 4-bromo-*p*-terphenyl

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transfer [1–4] also generally refer to T_1 free energies that include entropy differences between T_1 and S_0 . As noted above, phosphorescence measurements only provide triplet enthalpies. It is possible to determine triplet state *free energies* in solution by measuring the equilibration between the triplet–triplet (T–T) absorptions of reference and unknown compounds in pulse photolysis experiments [5–13]. Herein we report T_1 free energies (E_T) measured by laser flash photolysis for 60 triplet energy donors and acceptors in ethyl acetate at 295 K.

While the designation as a donor or an acceptor is somewhat arbitrary, we have chosen a small energy gap between the lowest excited singlet (S_1) and triplet states as the main criterion for designation as a donor. This ensures that most of the energy absorbed to produce the S_1 will be available as T_1 energy. Donors also generally have high ($S_1 \rightarrow T_1$) intersystem crossing quantum yields (Φ_T), which are also reported herein. Because of these two properties, the donors can generally serve as efficient photochemical sensitizers. Many of the xanthone, thioxanthone and ketocoumarin type donors of this study have been used as sensitizers in optical recording media [14]. The acceptors may function as useful co-sensitizers, which at high concentrations can assist in the transfer of triplet energy from a sensitizer to a lower-energy acceptor, as also discussed in Ref. [14].

The establishment of a scale of E_T values requires a suitable reference triplet energy. It was possible to measure the phosphorescence from naphthalene at 295 K in 1,1,2-trichlorotrifluoroethylene/ethyl acetate mixtures. Based on the negligible Stokes' shift between T_1/S_0 absorption and emission for naphthalene [15], this measurement directly provided a value for the T_1 enthalpy of naphthalene. Naphthalene is a relatively rigid molecule (reflected in the low Stokes' shift) that is expected to have a minimal entropy difference between S_1 and T_1 . This is reinforced by a measured ΔS of ~ 0.0 for equilibration of naphthalene and rigid chrysene triplets [5]. With the assumption of a negligible $-T\Delta S$ contribution to E_T , the phosphorescence of naphthalene at 295 K (see below) provided a reference thermodynamic triplet energy of 60.5 kcal/mol.

Ethyl acetate was selected as a solvent because it has better solvating properties than alkanes and because it is less likely to participate in triplet energy transfer with some high-energy donors and acceptors than aromatic solvents like benzene and toluene.

2. Experimental

2.1. Materials

HPLC grade 99.9% ethyl acetate and 99.9% 1,1,2-trichlorotrifluoroethane (CFC-113) were used without further purification. Most of the triplet energy donors and acceptors are either commercially available or were synthesized as described elsewhere [14,16]; a few were obtained from the Chemical Library of the Eastman Kodak Company. Samples were purified by recrystallization, column chromatography and distillation as necessary. Donor and acceptor structures are pro-

vided in Fig. 4, and full names are provided in the supplementary information.

2.2. Laser flash photolysis measurements

Triplet–triplet absorption spectra and extinction coefficients, triplet equilibria and triplet lifetimes (τ_T) were measured using a nanosecond laser flash photolysis apparatus described elsewhere [17]. A Lambda Physik Lextra 50 XeCl excimer laser was used for direct sample excitation at 308 nm or to pump a Lambda Physik 3002 dye laser, providing approximately 7 ns high-intensity pulses. Most measurements were carried out using either 343 nm excitation (with *p*-terphenyl as the laser dye) or 400 nm excitation (with diphenylstilbene). Transient absorptions were monitored at 90° to the laser excitation using pulsed xenon lamps, timing shutters, a monochromator and a photomultiplier tube for kinetic measurements or a diode array detector for obtaining transient absorption spectra. For kinetic analyses the signal from the photomultiplier tube was directed into a Tektronix TDS 620 digitizing oscilloscope and then to a computer for viewing, storage and analysis. Typically, attenuated beam energies were less than 1 mJ pulse⁻¹ (to minimize ground state depletion, photochemical reactions, light absorption by products, and T–T annihilation). Data were averaged over approximately 20 pulses. For most measurements, samples in sealed 1 cm quartz cells were deoxygenated by argon bubbling.

2.3. Luminescence measurements

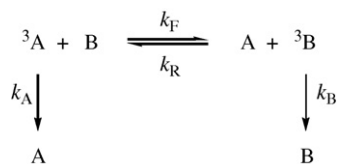
Phosphorescence spectra and 0,0 triplet energies, E_P , of nearly all donors and many acceptors of this study were measured in ethyl acetate at ambient temperature (~ 295 K) using a Fluorolog-3 spectrofluorometer (Jobin Yvon, Horiba). Fairly large slit widths (1–3 nm) were typically required on both excitation and emission monochromators to help offset low phosphorescence efficiencies resulting from quenching by impurities and other nonradiative decay processes. Molecules with enhanced spin–orbit coupling associated with heavy atoms or with $n\pi^*$ T_1 states were generally more suited to room temperature phosphorescence measurements. For some molecules, phosphorescence efficiencies were substantially improved by the external heavy atom effect produced by addition of small amounts (5–10%) of butyl iodide or by use of CFC-113 as a co-solvent.

A rotating-sector phosphorescope was also used in some cases to aid in distinguishing weak long-lived phosphorescence from prompt fluorescence. Some comparative phosphorescence measurements were also carried out in frozen ethyl acetate at 77 K.

3. Methods

3.1. Triplet energies

Thermodynamic triplet energies were determined via procedures similar to those originally used by Kikuchi et al. [8] and



Scheme 1.

Kira and Thomas [9]. The method relies on the equilibration between two triplet species (${}^3\text{A}$ and ${}^3\text{B}$) and their ground states (A and B) in solution according to Scheme 1, where k_{F} and k_{R} are respective forward and reverse energy transfer rate constants, and k_{A} and k_{B} are rate constants for decay of ${}^3\text{A}$ and ${}^3\text{B}$ to their respective ground states.

Under conditions where k_{A} and k_{B} are small relative to $k_{\text{F}}[\text{B}]$ and $k_{\text{R}}[\text{A}]$, after a sufficient equilibration time, the following relationship between ${}^3\text{A}$ and ${}^3\text{B}$ is established, where K is the equilibrium constant:

$$\frac{[\text{A}][{}^3\text{B}]}{[{}^3\text{A}][\text{B}]} = \frac{k_{\text{F}}}{k_{\text{R}}} = K \quad (1)$$

The free energy difference (ΔG) for the equilibrium is then given by

$$\Delta G = \Delta G_{\text{T}}(\text{B}) - \Delta G_{\text{T}}(\text{A}) = -RT \ln K \quad (2)$$

where $\Delta G_{\text{T}}(\text{A})$ and $\Delta G_{\text{T}}(\text{B})$ are the differences in free energy between the triplet states and ground states of A and B, respectively, and hereafter referred to as $E_{\text{T}}(\text{A})$ and $E_{\text{T}}(\text{B})$. If the value of either $E_{\text{T}}(\text{A})$ or $E_{\text{T}}(\text{B})$ can be established independently, then the value of the other can be calculated from ΔG . From a practical standpoint reliable E_{T} values can be obtained by this procedure for $|\Delta G|$ values up to ~ 3 kcal/mol, if the higher- E_{T} component of the pair is sufficiently soluble (~ 0.01 – 0.10 M).

It has been common [8–13] to assume that entropy contributions to E_{T} values are relatively small, such that E_{T} essentially represents the enthalpy difference between the triplet state and ground state and may be compared to enthalpy differences from phosphorescence measurements. However, as noted above and further discussed below, this is not necessarily the case when the chromophore possesses considerable rotational or conformational freedom. We have used herein the more conventional symbol, E_{T} , instead of ΔG_{T} to represent triplet energy, while recognizing that E_{T} encompasses both entropy and enthalpy differences between T_1 and S_0 .

It is instructive to consider in more detail the conditions that are required to establish an equilibrium in which the relative concentrations of ${}^3\text{A}$ and ${}^3\text{B}$ provide accurate values of K and of E_{T} . Analogously to the treatment in Ref. [18], Eq. (1) will apply if both k_{A} and $k_{\text{B}} \ll (k_{\text{F}}[\text{B}] + k_{\text{R}}[\text{A}])$, which can be achieved at suitably high concentrations of A and/or B. The time required to reach equilibrium is $\gg 1/(k_{\text{F}}[\text{B}] + k_{\text{R}}[\text{A}])$.

An alternative analysis provided in the supplementary information illustrates that ${}^3\text{A}$ and ${}^3\text{B}$ may be in apparent quasi-equilibrium, i.e., their ratio may remain constant with time, even if the conditions of Eq. (1) are not satisfied. Thus, it is important that the criteria, k_{A} and $k_{\text{B}} \ll (k_{\text{F}}[\text{B}] + k_{\text{R}}[\text{A}])$, be satisfied. This can usually be verified by determining that calculated values of

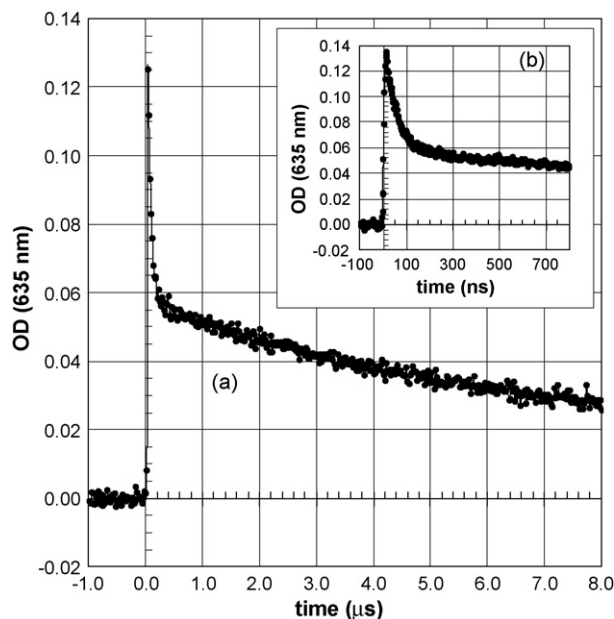


Fig. 1. Decay (a) over 8 μs and (b) over 800 ns of ${}^3\text{2MeOTX}$ at 635 nm in an Ar-purged ethyl acetate solution of 1 mM ${}^3\text{2MeOTX}$ plus 10 mM NAP excited by 7 ns pulses of 343 nm laser light.

K remain essentially constant as the concentrations of A and B are changed.

It is also possible that an encounter between a triplet and ground state molecule leaves both in the ground state [8]. In principle (see supplementary information) this could lead to apparent K values that are independent of A and B concentrations, even if Eq. (1) is not satisfied. Perhaps the best indication that equilibration between ${}^3\text{A}$ and ${}^3\text{B}$ is fast relative to triplet decay processes and that Eq. (1) applies can be provided by kinetic measurements. As shown in Fig. 1, kinetic plots of the decay of T–T absorption showed a bi-exponential decay with a clear distinction between a rapid pre-equilibrium decay and a slower quasi-equilibrium decay when the above criteria were met.

While it was not required for the measurements herein, it is nevertheless possible to extract accurate values for K and E_{T} from kinetic measurements even when k_{A} and k_{B} are not $\ll (k_{\text{F}}[\text{B}] + k_{\text{R}}[\text{A}])$. This may be accomplished by a full kinetic analysis of triplet decay [13,19,20], preferably at more than one set of concentrations. This procedure has been recently applied to both electron transfer equilibria [21] and to triplet energy transfer [17], and is reviewed in the supplementary information.

We have used three methods to determine K and E_{T} values from transient absorption measurements.

3.1.1. Method I: sensitizer/acceptor triplet equilibration

In this method a solution of a reference (here called A) with a known E_{T} and a target molecule (B) with unknown E_{T} was excited by laser pulses. At least one of A and B must be a sensitizer that absorbs at the excitation wavelength and has a substantial Φ_{T} to produce a suitable T–T absorption signal. Transient absorption spectra were obtained at successive delay times until the ratio of T–T absorptions of ${}^3\text{A}$ and ${}^3\text{B}$ remained con-

stant, indicating that selected concentrations of A and B were sufficient to attain quasi-equilibrium. Under these conditions Eq. (1) usually applies. Kinetic measurements were used to confirm the applicability of Eq. (1).

To determine $[^3A]$ and $[^3B]$, wavelengths a and b may be selected at which respective 3A and 3B absorptions predominate. It can be shown that $[^3A] = (OD^a - xOD^b)/(\epsilon_{3A}^a - x\epsilon_{3A}^b)$ and $[^3B] = (OD^b - yOD^a)/(\epsilon_{3B}^b - y\epsilon_{3B}^a)$ where ϵ_{3A} and ϵ_{3B} are extinction coefficients, $x = \epsilon_{3B}^a/\epsilon_{3B}^b$ and $y = \epsilon_{3A}^b/\epsilon_{3A}^a$. Furthermore, at low pulse energies $[A] = [A]_0 - [^3A] \cong [A]_0$ and $[B] = [B]_0 - [^3B] \cong [B]_0$, where $[A]_0$ and $[B]_0$ are the initial concentrations of A and B prior to pulse excitation. Alternatively, the entire quasi-equilibrium T–T absorption spectrum may be fit to determine relative concentrations of 3A and 3B [22]. The unknown triplet energy is calculated from Eq. (2). In practice relative ϵ_{3A} and ϵ_{3B} values may be used. The determination of extinction coefficients is described below.

3.1.2. Method II: co-sensitization

This method is a variant of method I in which a sensitizer whose triplets can be rapidly quenched is used to excite a pair of triplet energy acceptors comprising a reference, A, and an acceptor of unknown triplet energy, B. This method was useful for determining E_T values of acceptors for which a sensitizer with a significantly different T–T absorption spectrum or a sufficiently close E_T could not be identified. The concentrations of A and B can usually be selected so that establishment of quasi-equilibrium is rapid relative to decay of the triplets. To ascertain the establishment of quasi-equilibrium, transient absorption spectra were obtained at successive delay times until the ratio of T–T absorptions of 3A and 3B remained constant. Under these conditions Eq. (1) usually applies. Concentrations of A and B can be varied to improve accuracy and verify the validity of Eq. (1). As with method I, relative extinction coefficients for 3A versus 3B at two or more wavelengths are needed.

3.1.3. Method III: donor triplet absorption

This method is attractive because it requires no knowledge of relative or absolute extinction coefficients and thereby removes any error associated with their uncertainty. If in a solution of a donor (here called A) and an acceptor (B), either of which can be the E_T reference, only A absorbs significantly at the laser excitation wavelength (which is true for many combinations of donors and acceptors reported here), and a wavelength exists at which only 3A absorbs appreciable analyzing light (which is true for xanthone, thioxanthone and ketocoumarin donors with many acceptors), then at quasi-equilibrium (QE):

$$[^3B] = [^3A]_0 - [^3A] = \frac{OD_0 - OD_{QE}}{\epsilon_{3A}} \quad \text{and} \quad [^3A] = \frac{OD_{QE}}{\epsilon_{3A}} \quad (3)$$

Here $[^3A]_0$ is the concentration of 3A immediately after the laser pulse before significant quenching by B has occurred, OD_0 the initial absorbance of 3A at the wavelength where only it absorbs and OD_{QE} is the absorbance at that wavelength at QE. The values of OD_0 and OD_{QE} are best obtained from kinetic

plots of 3A decay. Eq. (3) applies as long as QE can be attained before significant triplet decay has occurred or if OD_{QE} can be extrapolated to that point. Under these commonly obtainable conditions Eq. (4) applies such that the knowledge of extinction coefficients is unnecessary.

$$K = \frac{[A][^3B]}{[B][^3A]} = \frac{[A](OD_0 - OD_{QE})}{[B]OD_{QE}} \quad (4)$$

Again at low pulse energies $[A] = [A]_0$ and $[B] = [B]_0$. This type of experiment is best performed at different A and B concentrations, which can confirm that residual optical densities are due to QE levels of 3A rather than absorption by 3B , impurity triplets or photoproducts at the analyzing wavelength. As in methods I and II, it is desirable that reasonably high concentrations of A and B (especially the higher- E_T component) be used, such that the establishment of QE is rapid relative to triplet decay. An example of suitable kinetic behavior is provided below.

3.2. Measurement of ϵ values for T–T absorption

Three methods were also used to measure extinction coefficients, ϵ , for T–T absorption. The first method is similar to that described previously [23,24] and requires that the target molecule (X) absorbs negligible excitation light and has a lower triplet energy than that of a reference, such as benzophenone (BP). Optical densities at the T–T absorption maxima were compared at equal laser intensities for a solution of BP only and a solution of an equal [BP] plus a sufficient amount (e.g., 5 mM) of X to fully quench 3BP by energy transfer before significant triplet decay has occurred. The extinction coefficient for the target triplet, ϵ_{3X} , is then equal to $\epsilon_{3BP} OD_{3X}/OD_{3BP}$, where OD_{3X} and OD_{3BP} refer to the optical densities of X and BP triplets at their respective absorption maxima. This method requires knowledge of the extinction coefficient for triplet BP, ϵ_{3BP} . We have used an ϵ_{3BP} of $7200 \text{ M}^{-1} \text{ cm}^{-1}$ in ethyl acetate. This is based on the average of previously reported values in benzene [23–25] and our measurement of a slightly lower ϵ_{3BP} in ethyl acetate than in benzene. All of the ϵ values provided herein are thus relative to the ϵ_{3BP} reference. It should be pointed out that if this value is not accurate, the E_T and Φ_T values reported here are unaffected, because they depend only on relative extinction coefficients. This method was useful for most of the acceptors because they do not absorb the 343 nm laser excitation light. For acceptors that absorb at 343 nm, it was preferable to use another reference donor (evaluated by the method below) that could be excited at 400 nm, where acceptor absorption is negligible. Laser power was kept low to avoid competitive absorption of laser light by triplets or photoproducts, and no laser power dependence was observed.

The second method of measuring extinction coefficients was most applicable to donors that absorb at the laser excitation wavelength. This method also involves comparison to the triplet extinction coefficient of a reference molecule, usually BP. Separate solutions of the reference (BP) and target donor (X) of equal optical density were prepared and excited with laser pulses of

equal intensity, and the optical densities due to T–T absorption were measured at their respective maxima. The T–T extinction coefficient of the donor is then given by Eq. (5). For these calculations Φ_T for BP was taken as 1.0. This method requires knowledge of Φ_T for the donor, which was obtained as discussed below.

$$\varepsilon_{3X} = \varepsilon_{3BP} \left(\frac{OD_{3X}}{OD_{3BP}} \right) \left[\frac{\Phi_T(X)}{\Phi_T(BP)} \right] \quad (5)$$

A third method of measuring extinction coefficients was applied to some of the thioxanthone and xanthone donors and served as a check of the second method. These molecules show no S_0 absorption near the T–T absorption maxima and very little T–T absorption in the region of the S_0 absorption maxima. This allows the T–T ε values to be determined by comparing the bleaching of ground state absorption (for which ε has been measured and which produces negative optical densities relative to baseline) to the rise of T–T absorption immediately after the laser pulse. This method also required a knowledge Φ_T values (see below). It provided ε values that agree with those of the second method within about 10%.

A detailed review of methods for the measurement of T–T extinction coefficients is provided in Ref. [25a].

3.3. Triplet quantum yield measurements

Intersystem crossing quantum yields, Φ_T , for donors were measured by a technique previously described by Scaiano et al. [26], which has the advantage over some prior measurements [27–29] in that it does not require ε values. Φ_T values were obtained by comparing the intensity of T–T absorption of an appropriate triplet energy acceptor (A) produced by laser flash excitation of solutions of A plus (a) the target donor (X) and (b) benzophenone (BP) reference at equal optical densities under conditions where quenching of 3X and 3BP by A is quantitative. An acceptor was selected that does not absorb at the laser excitation wavelength. The target donor quantum yield was then calculated from $\Phi_T(X) = \Phi_T(BP) OD_{3A}(X)/OD_{3A}(BP)$. As is customary, $\Phi_T(BP)$ for benzophenone was taken as unity.

Acceptors had to be chosen with substantially lower triplet energies than those of BP and X to ensure rapid and full quenching of the donor triplets. Because of its sharp T–T absorption spectrum, naphthalene (NAP) was the preferred acceptor for target donors with $E_T \geq 62$ kcal/mol. For donors with E_T values between ~ 57 and 62 kcal/mol either 1,4-dibromonaphthalene or dibenzosuberone was used, and 2-phenylindene was used for donors with E_T between ~ 52 and 57 kcal/mol. For donors with E_T values between ~ 48 and 52 kcal/mol, 400 nm laser excitation was used with methyl-1-pyrenebutyrate as the acceptor and 2-methoxythioxanthone as the Φ_T reference. All of the acceptors have T–T ε values exceeding $10^4 \text{ M}^{-1} \text{ cm}^{-1}$. Thus, it was necessary to use low laser power to minimize competitive absorption of the excitation light by triplets.

4. Results and discussion

4.1. Thermodynamic triplet energies, E_T

The use of the kinetic measurements of method III (donor triplet absorption) to obtain E_T values is exemplified by Fig. 1a and b. These figures show the decay of T–T absorption at 635 nm due to triplet 2-methoxythioxanthone ($^32\text{MeOTX}$) at two time scales in a pulsed (343 nm), argon-purged solution of 1 mM 2MeOTX plus 10 mM NAP. Only 2MeOTX absorbs the laser light and only $^32\text{MeOTX}$ absorbs at the analyzing wavelength of 635 nm. Fig. 1a shows a sharp distinction between the very rapid pre-equilibrium quenching of $^32\text{MeOTX}$ by NAP to establish QE and the slow decay of the resulting QE blend of triplets. A fit of the slow QE decay allowed extrapolation to $t=0$ providing OD_{QE} for use in Eq. (4), above. To obtain OD_0 for Eq. (4) it was best to use the initial OD from a decay trace obtained at a shorter time scale like that in Fig. 1b. Because the data were recorded digitally at fixed time intervals, measurements at longer time scales like Fig. 1a may miss the point(s) corresponding to the initial maximum OD. An analysis of these data provided a ΔG of 1.2 kcal/mol for the transfer of energy from $^32\text{MeOTX}$ to NAP and an E_T of 59.3 kcal/mol for 2MeOTX .

Fig. 2 illustrates the use of T–T absorption measurements at QE to determine E_T values according to method I (sensitizer/acceptor triplet equilibration). In this example, argon-purged ethyl acetate solutions containing 0.45 or 0.9 mM of 2MeOTX sensitizer with either 5 or 10 mM 1-methylphenanthrene (1MP) acceptor were excited with 343 nm laser pulses, and their transient absorption spectra were measured after 1 μs . Kinetic measurements similar to those in Fig. 1 indicated that this time delay was sufficient for QE to be achieved. The band at 635 nm corresponds to T–T absorption

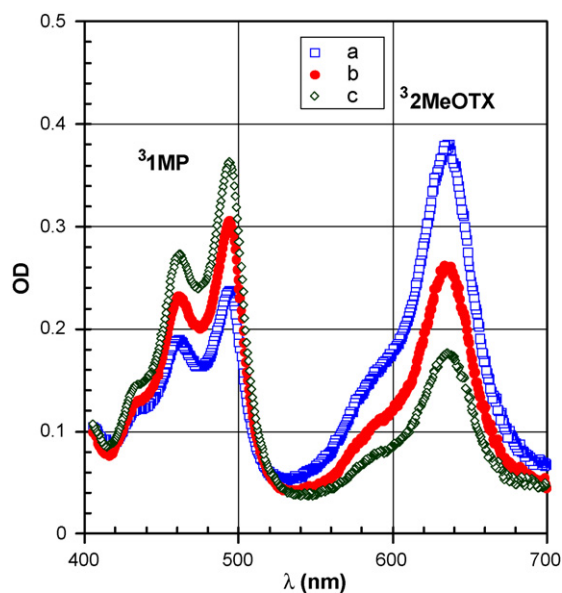


Fig. 2. Equilibrated T–T absorption spectra measured 1 μs after laser excitation at 343 nm of Ar-purged ethyl acetate solutions of (a) 0.9 mM 2MeOTX + 5 mM 1MP, (b) 0.45 mM 2MeOTX + 5 mM 1MP and (c) 0.45 mM 2MeOTX + 10 mM 1MP.

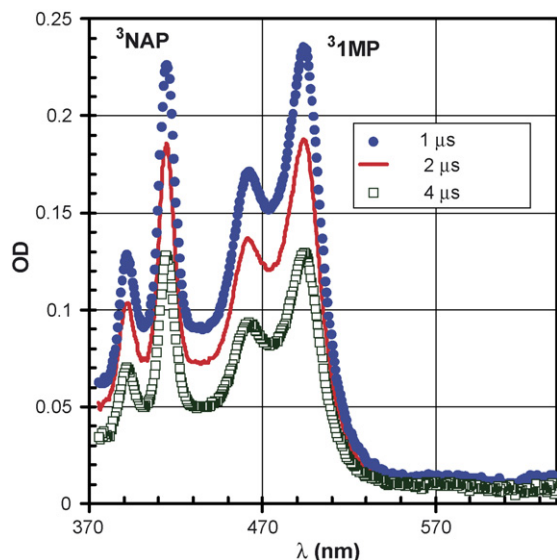


Fig. 3. Equilibrated T–T absorption spectra measured at 1, 2 and 4 μs after pulsed laser excitation at 343 nm of an argon-purged ethyl acetate solution of 10 mM BP with 4 mM NAP and 5 mM IMP.

by ${}^3\text{2MeOTX}$, and that at 493 nm is due to ${}^3\text{1MP}$. An analysis of the data in Fig. 2 indicated that ΔG for the transfer of triplet energy from 2MeOTX to 1MP is 1.2 kcal/mol. This yielded an E_T of 60.5 kcal/mol for 1MP based on the E_T value for 2MeOTX of 59.3 kcal/mol determined above.

The use of method II (co-sensitization) to determine E_T values is illustrated by the T–T absorption spectra in Fig. 3. In this example, an argon-purged solution containing 10 mM benzophenone (BP) sensitizer plus 4 mM NAP and 5 mM IMP was excited with 343 nm laser pulses. The transient absorption spectra at various delay times after the laser pulse are shown in Fig. 3. The BP triplets were rapidly quenched by the acceptors, and no T–T absorption due to ${}^3\text{BP}$ at 530 nm is evident. The fact that the relative T–T absorptions of ${}^3\text{NAP}$ (at 413 nm) and ${}^3\text{1MP}$ (at 493 nm) remain constant with time illustrates that QE has been achieved by 1 μs . An analysis of these data yielded a ΔG of 0.0 kcal/mol and an E_T for 1MP of 60.5 kcal/mol.

Thermodynamic E_T values obtained according to the above procedures are listed for 23 triplet energy donors or sensitizers in Table 1 and for 37 triplet energy acceptors in Table 2. The E_T values for the donors span a range of about 22 kcal/mol and the acceptor E_T values span a range of 26 kcal/mol, both centered around the E_T of NAP. Donor and acceptor structures are given in Fig. 4. Contracted names are used for some of the donors and acceptors in Tables 1 and 2. Full names for these are provided in the supplementary information. Most of the E_T values in Tables 1 and 2 were measured by both methods I and III, described above. Many values were also measured by method II. Error estimates are also provided, which tend to increase as E_T values diverge from the NAP reference value of 60.5 kcal/mol.

Many of the E_T determinations in Tables 1 and 2 were carried out versus more than one reference as a check on the consistency of the results. Tables S1 and S2 in the supplementary information provide relationship diagrams or triplet energy ladders, which show the reference/target pairs that were equilibrated to deter-

mine E_T values. Discussion of the significance of some of the E_T values is provided in Section 4.5.

4.2. Triplet lifetimes, τ_T

The triplet lifetimes listed in Tables 1 and 2 serve to illustrate that triplet decay is sufficiently slow to allow triplet equilibration in which k_A and k_B are small relative to $k_F[\text{B}]$ and $k_R[\text{A}]$ of Scheme 1. These lifetimes are not necessarily intrinsic, because they may be affected, at least slightly, by quenching by residual oxygen or by trace impurities in the samples or solvent, by T–T annihilation, and by quenching by ground state or by traces of photoproducts. We have observed slight increases in τ_T at lower laser powers in some cases, reflecting reduced T–T annihilation. This is particularly noticeable for triplets with lower ϵ values that require higher triplet concentrations for suitable optical densities. In some cases hydrogen abstraction from solvent molecules may also reduce τ_T . This appeared to be true for BP and xanthone, although the amounts of ketyl radical products observed indicated that this was not the major decay pathway for either triplet. In ethyl acetate *without* added quencher $\sim 25\%$ of ${}^3\text{BP}$ decay led to formation of ketyl radical ($\lambda_{\text{max}} = 548 \text{ nm}$, $\epsilon \sim 4000 \text{ M}^{-1} \text{ cm}^{-1}$).

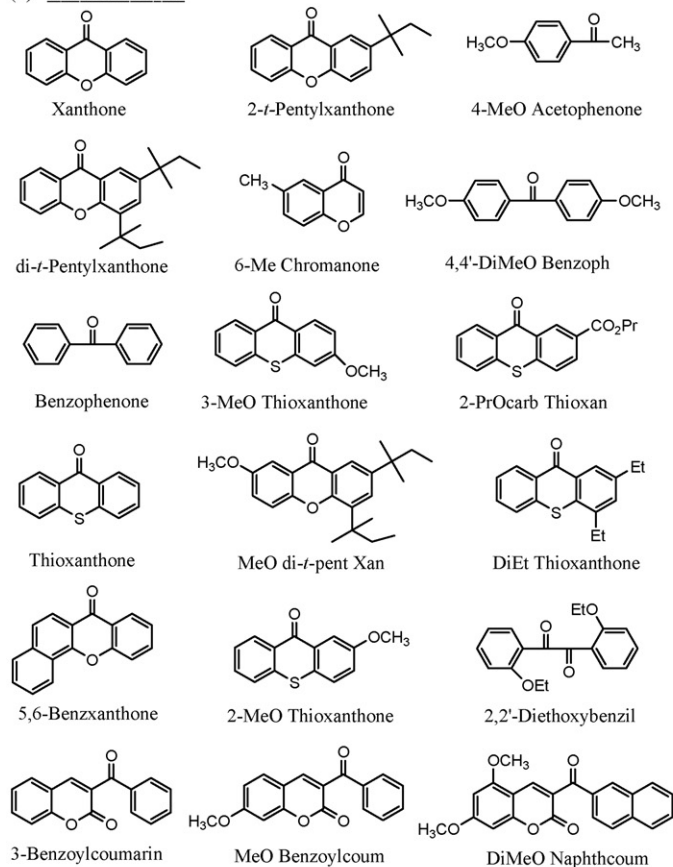
4.3. Donor triplet quantum yields, Φ_T

Intersystem crossing quantum yields, Φ_T , for the donor/sensitizers in Table 1 are generally high, with most approaching unity. Values are reasonably close to literature values in other solvents [25b]. Φ_T values for 2MeOTX and 2,4-diethylthioxanthone are the same within experimental error as those measured via sensitized isomerization of *trans*-stilbene in ethyl acetate [17]. The Φ_T value for 3,3'-carbonylbis(7-diethylaminocoumarin) (BDEAC) of 0.10 is surprisingly low, considering the reported value of 0.92 in benzene [16]. The low Φ_T in ethyl acetate is not accompanied by strong fluorescence; instead it appears to reflect rapid nonradiative decay of S_1 to S_0 , probably via enhanced charge transfer coupling in the more polar ethyl acetate. Consistent with this hypothesis, we measured a Φ_T of 0.9 for BDEAC in less polar toluene by the same technique. The somewhat low Φ_T of 0.60 for 3,3'-carbonylbis(5,7-dipropoxycoumarin) in ethyl acetate may have the same origin.

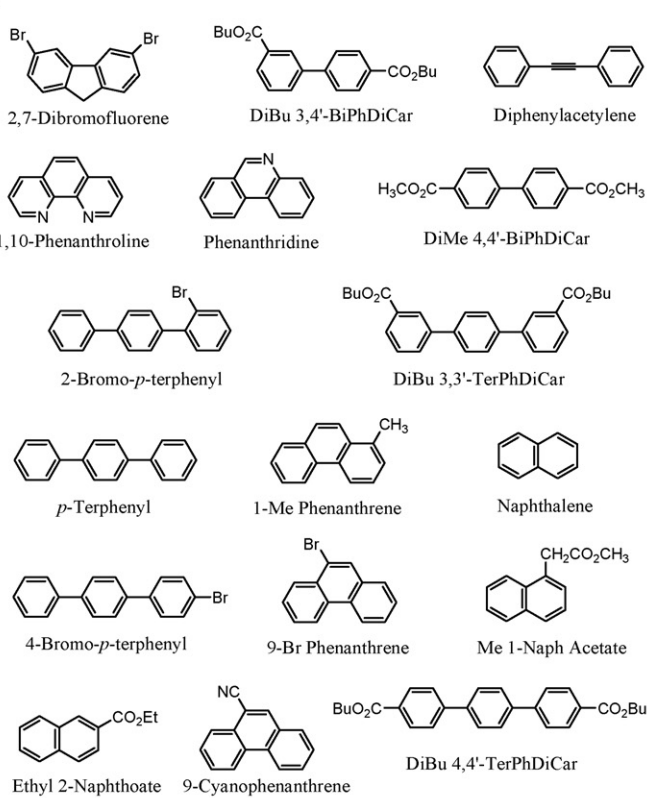
4.4. Triplet–triplet absorption λ_{max} and ϵ_{max} data

Triplet–triplet absorption maxima (λ_{max}) and associated extinction coefficients (ϵ_{max}) are provided in Tables 1 and 2. All of the xanthone and thioxanthone donors showed strong T–T absorption in the vicinity of 630–650 nm, where most of the acceptors have little or no T–T absorption. The ketocoumarins also showed a secondary absorption band near 700 nm that was somewhat weaker than the absorption maximum in Table 1. Due to their high ϵ_{max} values, that can exceed $10^5 \text{ M}^{-1} \text{ cm}^{-1}$, many of the polyphenyl acceptors represent very good probes for energy transfer processes.

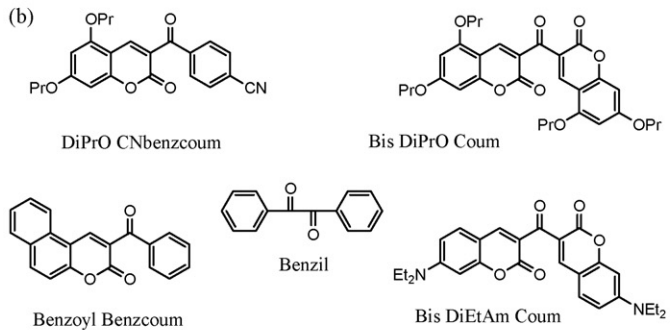
(a) Donor/Sensitizers



(c)



(b)



(d)

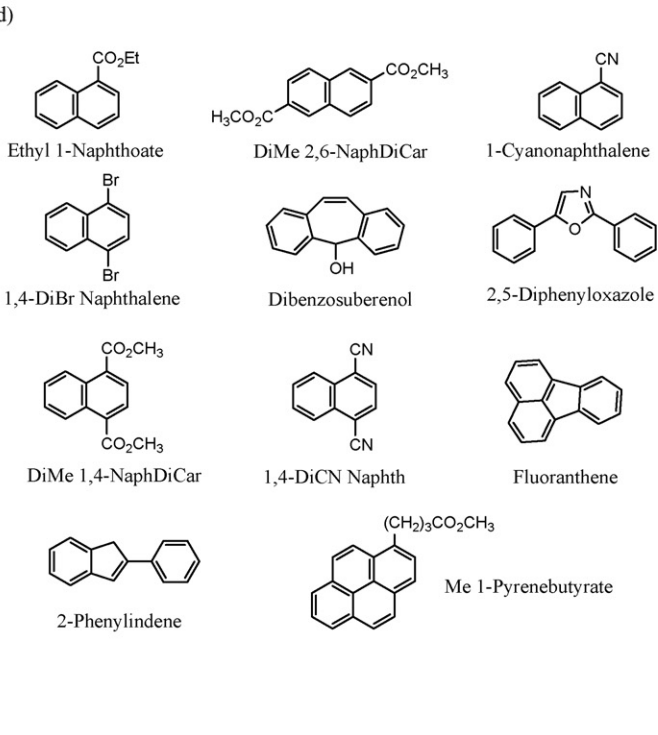


Fig. 4. Donor and acceptor structures.

Table 1
Donor/sensitizer parameters in EtOAc @ 295 K

Donor/sensitizer	E_T (thermo.) (kcal/mol)	E_P (phos.) (kcal/mol)	τ_T (μ s)	Φ_T (± 0.05)	T–T absorption	
					λ_{\max} (nm)	ϵ_{\max} ($M^{-1} \text{ cm}^{-1}$) ($\pm\%$)
Xanthone	73.2 \pm 0.4	$\sim 73^c$	1.2	0.90	633	9,500 \pm 20
2- <i>t</i> -Pentylxanthone	71.3 \pm 0.2	$\sim 71^c$	5	0.99	642	19,000 \pm 15
4-MeO acetophenone	70.9 \pm 0.3	70.9	9	0.95	376	10,000 \pm 15
Di- <i>t</i> -Pentylxanthone	69.9 \pm 0.2	69.9 ^c	8	0.99	654	17,000 \pm 15
6-Me chromanone	69.8 \pm 0.3	–	5	0.90	424	6,000 \pm 15
4,4'-DiMeO benzoph	69.0 \pm 0.2	68.8	8	0.97	547	8,000 \pm 15
Benzophenone	68.7 \pm 0.1	68.2	4	1.00	526	7,200 \pm 10
3-MeO thioxanthone	67.0 \pm 0.2	67.0 ^d	13	1.00	634	22,000 \pm 15
2-PrOcarb thioxan	65.8 \pm 0.1	65.7 ^d	7	0.96	639	27,000 \pm 15
Thioxanthone	65.0 \pm 0.1	64.9 ^d	15	0.99	635	22,000 \pm 15
MeO di- <i>t</i> -pent Xan	64.6 \pm 0.1	64.5 ^c	22	0.97	643	19,000 \pm 15
DiEt thioxanthone	63.5 \pm 0.1	63.5 ^d	25	0.99	649	31,000 \pm 15
5,6-Benzoxanthone	61.3 \pm 0.1	60.7	20	0.97	438	7,500 \pm 15
2-MeO thioxanthone	59.3 \pm 0.1	–	24	0.97	636	24,000 \pm 15
2,2'-Diethoxybenzil	58.9 \pm 0.3	50.9	10	–	476	4,000 \pm 20
3-Benzoylcoumarin	58.4 \pm 0.2	$\sim 57^e$	2	0.85	414	7,500 \pm 15
MeO benzoylcoum	57.4 \pm 0.2	56.0	32	0.93	464	13,000 \pm 15
DiMeO naphthcoum	56.4 \pm 0.2	55.5	13	0.85	442	10,000 \pm 15
DiPrO CNbenzcoum	55.8 \pm 0.2	54.8	26	0.90	486	11,500 \pm 15
Bis DiPrO coum	55.2 \pm 0.3^a	55.1	24	0.60	459	10,500 \pm 15
Benzil	55.0 \pm 0.2	50.7	15	1.00	484	11,000 \pm 15
Benzoyl benzcoum	51.5 \pm 0.2	50.4 ^e	26	0.85	550	20,000 \pm 20
Bis DiEtAm coum	51.1 \pm 0.3^b	51.3 ^c	36	0.10 ^f	~ 508	14,500 \pm 25

The bold items are the thermodynamic triplet energies

^a Statistically corrected $E_T = 55.6$ kcal/mol for this bis sensitizer.

^b Statistically corrected $E_T = 51.5$ kcal/mol for this bis sensitizer.

^c In CFC-113/EtOAc + 5% BuI; estimated from maximum at 298 K and 0,0 vs. maximum offset at 77 K.

^d Estimated from the maximum at 298 K and the 0,0 vs. maximum offset at 77 K.

^e In CFC-113/EtOAc.

^f Increases to 0.9 in toluene.

Errors in the *relative* extinction coefficients are generally no more than $\sim 10\%$, the remaining ϵ_{\max} error in Tables 1 and 2 being due to uncertainty in ϵ_{3BP} . A 10% error in the relative extinction coefficient translates to a 10% error in the calculated ratio of triplet concentrations, which (via $-RT \ln K$) translates to only ~ 0.05 kcal/mol uncertainty in E_T .

Allowing for solvent effects, the ϵ_{\max} values in Tables 1 and 2 are in reasonable agreement with those compiled by Carmichael and Hug [25a], where comparisons are possible.

4.5. Phosphorescence triplet energies, E_P

Triplet enthalpies, E_P , obtained from phosphorescence measurements at an ambient temperature of about 295 K are listed for most donor/sensitizers in Table 1 and for many acceptors in Table 2. These values correspond to vertical 0,0 transition enthalpies from the lowest vibrational level of the dominant vibrational progression in T_1 to the lowest vibrational level of S_0 . Instances in which heavy atom-containing butyl iodide was added or 1,1,2-trichlorotrifluoroethane (CFC-113) was used as a co-solvent to enhance phosphorescence intensity are indicated in the footnotes of Tables 1 and 2. CFC-113 may increase the phosphorescence intensity due to less impurity quenching and/or by a mild heavy atom effect. For the xanthenes, thioxanthenes and some of the

brominated acceptors the 0,0 phosphorescence bands were poorly resolved at 295 K. In these instances E_P values were estimated from the λ_{\max} values at 295 K and the offset between the λ_{\max} and 0,0 band at 77 K. For the xanthenes, butyl iodide was also added to the ethyl acetate solvent to enhance 0,0 phosphorescence at 77 K. The external heavy atom effect tends to enhance the totally symmetric 0,0 vibrational modes [30]. All triplet energies were insensitive to excitation wavelength at 295 K, reflecting the full relaxation of both the emitter and the medium prior to emission.

As discussed above, the E_P value for naphthalene (NAP) at 295 K is assumed to equal E_T and thereby serves as the reference thermodynamic triplet free energy. Fig. 5 compares the phosphorescence spectra of NAP in 1:1 ethyl acetate:CFC-113 at 295 K and in ethyl acetate at 77 K. The 0,0 energy of the 295 K phosphorescence is only very slightly (~ 0.3 kcal/mol) bathochromic to that at 77 K. This difference may be due simply to solvent polarizability differences and/or differences in solvent dipole relaxation at the two temperatures, and suggests that the T_1 and S_0 geometries are quite similar for NAP. If the relaxed geometry of T_1 were significantly different from the equilibrium S_0 geometry, then the relaxed T_1 energy would be substantially lower and the $T_1 \rightarrow S_0$ vertical transition energy would be different at 295 K and 77 K due to differences in T_1 relaxation prior

Table 2
Acceptor parameters in EtOAc @ 295 K

Acceptor	E_T (thermo.) (kcal/mol)	E_P (phos.) (kcal/mol)	τ_T (μ s)	T–T Absorption	
				λ_{\max} (nm)	ϵ_{\max} ($M^{-1} \text{ cm}^{-1}$) (%)
Dimethyl phthalate	73.5 ± 0.2		7	~305	–
DiMe terephthalate	72.8 ± 0.2		3	~311	~20,000
Trimethyl trimellitate	71.5 ± 0.2		5	~311	–
Me 4-CNBenzoate	71.5 ± 0.2		3	~305	–
Dibenzofuran	69.4 ± 0.2		13	393	23,500 ± 15
2-Chlorobiphenyl	69.1 ± 0.2		25	356	19,000 ± 20
Me 9-fluorene-carbox	66.6 ± 0.2		13	373	25,000 ± 15
Biphenylacetate	66.5 ± 0.2		15	371	29,000 ± 20
4,4'-Dibromobiphenyl	64.6 ± 0.1	62.3 ^a	26	399	62,000 ± 15
2,7-Dibromofluorene	64.5 ± 0.1	64.2 ^a	9	411	47,000 ± 15
DiBu 3,4'-BiPhDiCar	63.8 ± 0.1		40	402	48,000 ± 15
Diphenylacetylene	62.9 ± 0.2		30	406	48,000 ± 15
1,10-Phenanthroline	62.7 ± 0.1		12	440	7,500 ± 15
Phenanthridine	62.7 ± 0.2	62.4 ^b	20	462	7,500 ± 15
DiMe 4,4'-BiPhDiCar	61.7 ± 0.1		28	419	85,000 ± 15
2-Bromo- <i>p</i> -terphenyl	61.1 ± 0.3	55.8	26	466	60,000 ± 15
DiBu 3,3'-TerPhDiCar	60.6 ± 0.1		70	451	82,000 ± 15
<i>p</i> -Terphenyl	60.5 ± 0.2		45	445	81,000 ± 15
1-Me phenanthrene	60.5 ± 0.2		24	493	13,500 ± 15
Naphthalene	60.5 ± 0.0	60.5 ^c	22	413	15,000 ± 15
4-Bromo- <i>p</i> -terphenyl	59.8 ± 0.2	56.0	40	461	94,000 ± 20
9-Br phenanthrene	59.8 ± 0.2	59.8 ^a	26	480	11,000 ± 15
Me 1-naph acetate	59.5 ± 0.1		25	420	17,000 ± 15
Ethyl 2-naphthoate	59.0 ± 0.2	58.6 ^b	33	425	13,000 ± 15
9-Cyanophenanthrene	57.7 ± 0.1	57.5 ^b	26	489	8,000 ± 15
DiBu 4,4'-terPhDiCar	57.5 ± 0.1		75	499	100,000 ± 15
Ethyl 1-naphthoate	57.4 ± 0.1	56.8 ^b	23	443	8,500 ± 15
DiMe 2,6-naphDiCar	57.2 ± 0.2	56.2 ^b	27	442	13,000 ± 15
1-Cyanonaphthalene	57.2 ± 0.1	57.1 ^c	24	443	10,500 ± 15
1,4-DiBr naphthalene	56.9 ± 0.1	56.4 ^a	21	426	10,500 ± 15
Dibenzosuberenol	55.9 ± 0.3		28	423	22,000 ± 15
2,5-Diphenyloxazole	55.4 ± 0.3		25	493	16,000 ± 15
DiMe 1,4-naphDiCar	53.8 ± 0.3		22	467	6,000 ± 20
1,4-DiCN naphth	53.1 ± 0.2	52.5 ^b	22	458	6,000 ± 20
Fluoranthene	52.5 ± 0.3		23	394	6,500 ± 15
2-Phenylindene	51.2 ± 0.2		16	380	31,000 ± 15
Me 1-pyrenebutyrate	47.7 ± 0.3	47.5 ^b	28	416	17,500 ± 15

The bold items are the thermodynamic triplet energies

^a Estimated from the maximum at 295 K and the 0,0 vs. maximum offset at 77 K.

^b EtOAc + 5–10% BuI.

^c In CFC-113/ethyl acetate.

to emission. A very similar geometry for T_1 and S_0 further suggests similar bond orders and similar entropies in the ground and excited states.

Comparison of the E_T and E_P values in Tables 1 and 2 reveals that for rigid molecules the two are generally very similar throughout the range of triplet energies. For example, the E_T and E_P values for the rigid xanthone and thioxanthone sensitizers are within 0.2 kcal/mol. In contrast, for most of the less rigid ketocoumarin sensitizers, E_T values are about 1–1.5 kcal/mol greater than E_P values. For the polyphenyls, such as 4-bromo-*p*-terphenyl (4BTP), and for benzil and 2,2'-diethoxybenzil, all of which have considerable rotational freedom, E_T values are much larger than E_P values at 295 K.

The differences between E_T and E_P values reflect a combination of differences in T_1 versus S_0 entropies, which are not reflected in E_P , and differences in T_1 versus S_0 enthalpy

contributions to E_T and E_P arising from changes in equilibrium geometries. This may be better appreciated by referring to Fig. 6. This figure is a simplified representation of the electronic potential energies of T_1 and S_0 versus a bond length (R) or rotational angle (θ) that has a critical influence on energy. It is somewhat exaggerated for illustrative purposes. In reality, multi-dimensional potential energy surfaces determine the relationships between T_1 and S_0 . As we have defined it, $E_T = \Delta H_T - T\Delta S_T$, where ΔH_T is here defined as the T_1 enthalpy versus S_0 , and ΔS_T is defined as the T_1 entropy versus S_0 . As shown in Fig. 6, $E_P = \Delta H_T - E_R$, where E_R is the energy difference between S_0 in the T_1 equilibrium nuclear configuration and S_0 in its own equilibrium configuration. Thus, $E_T - E_P = E_R - T\Delta S_T$. A precise determination of the proportion of the ($E_T - E_P$) difference that is due to ΔS_T requires the measurement of E_T as a function of temperature [5–7]. Although

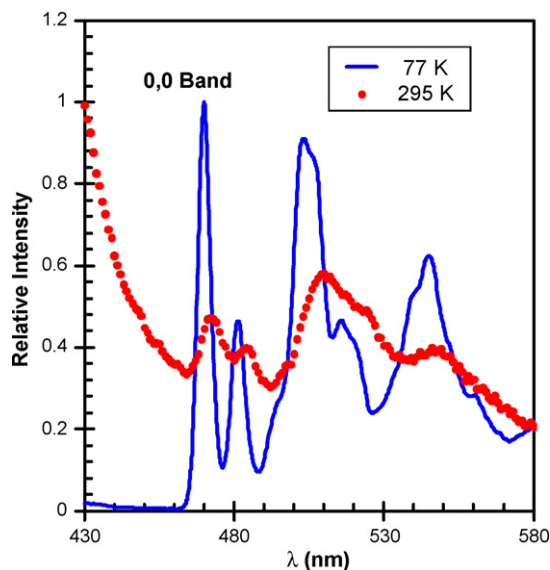


Fig. 5. Phosphorescence spectra of NAP at 77 K in ethyl acetate and at 295 K in argon-purged 1:1 ethyl acetate:1,1,2-trichlorotrifluoroethane.

we have not directly measured the entropic contributions to E_T , some insight may be gained by comparison of E_P values determined from phosphorescence spectra at 77 K and 295 K.

First consider 4BTP as representative of the polyphenyl acceptors, which have E_T values substantially (~ 2.5 – 5 kcal/mol) larger than E_P . The rotational freedom of the polyphenyl chromophores enhances the entropy and nuclear reconfiguration effects responsible for these energy differences. Phosphorescence spectra of many of the donors and acceptors at 77 K showed significant wavelength dependence due to a variety of frozen-in solvent sites and molecular configurations. However, very little wavelength dependence (± 0.1 kcal/mol) was observed for the phosphorescence spectra of 4BTP at 77 K. Phosphorescence spectra from 0.1 mM 4BTP in ethyl acetate at 77 K and in argon-purged ethyl acetate at 295 K are compared in Fig. 7. The difference between the 0,0 band energies (arrows) is 1.4 kcal/mol. The phosphorescence of 4BTP is insensitive to

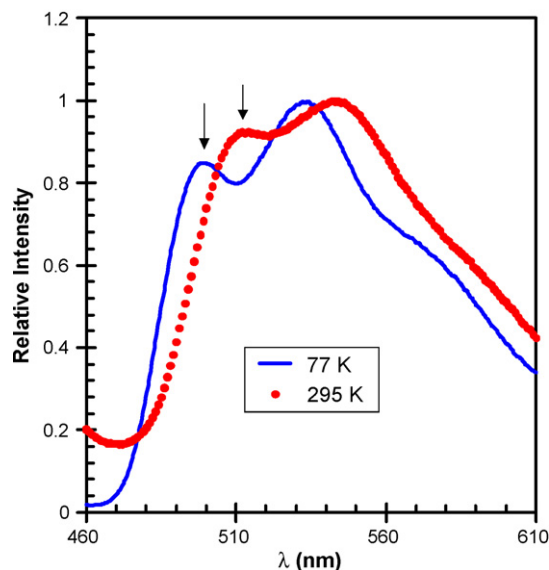


Fig. 7. Phosphorescence spectra of 0.1 mM 4BTP in ethyl acetate at 77 K and in argon-purged ethyl acetate at 295 K.

solvent polarity and only mildly sensitive to solvent polarizability, so the spectral shift in Fig. 7 is largely a consequence of emission from an unrelaxed or partially relaxed T_1 configuration at 77 K versus a fully relaxed T_1 configuration at 295 K.

At 295 K the phosphorescence corresponds to E_P , while at 77 K the emission energy is nearer to E_V , the vertical energy difference between T_1 and S_0 in the ground state geometry (Fig. 6). The critical coordinate θ in Fig. 6 represents torsional motions of the phenyl rings for polyphenyls [31]. If these are largely inhibited at 77 K, then the 0,0 phosphorescence maximum would correspond approximately to E_V . The difference between E_T and E_P for 4BTP at 295 K is 3.8 kcal/mol (Table 2). Since $\Delta H_T \leq E_V$ (Fig. 6), then if phosphorescence at 77 K occurs from a nuclear configuration close to the S_0 configuration, $E_R = \Delta H_T - E_P \leq (E_V - E_P)$ or ≤ 1.4 kcal/mol. With this interpretation most of the 3.8 kcal/mol difference between E_T and E_P would arise from a negative ΔS_T contribution, giving rise to a $-T\Delta S_T$ of ≥ 2.4 kcal/mol at 295 K. A T_1 entropy substantially less than that of S_0 is consistent with the negative ΔS_T values measured for biphenyl [5] and 4-methylbiphenyl [7] and with the anticipated more-planar, more-conjugated T_1 structures expected for polyphenyls [31].

Next consider the donor benzil for which $(E_T - E_P) = 4.3$ kcal/mol at 295 K (Table 1). Emission spectra of 5 mM benzil in (a) ethyl acetate at 77 K, (b) argon-purged ethyl acetate at 295 K and (c) air-saturated ethyl acetate at 295 K are compared in Fig. 8.

At 77 K the 0,0 maximum occurs at 55.3 kcal/mol with an excitation wavelength of 400 nm. However, the maximum shifts to lower energies by ~ 1 kcal/mol at 77 K as the excitation wavelength is increased toward 420 nm due to site and conformational variations. As with all donors and acceptors, the phosphorescence maximum of benzil at 295 K is independent of excitation wavelength. At 295 K the 0,0 maximum at 563 nm corresponds to an E_P of 50.7 kcal/mol, the same as previously reported in

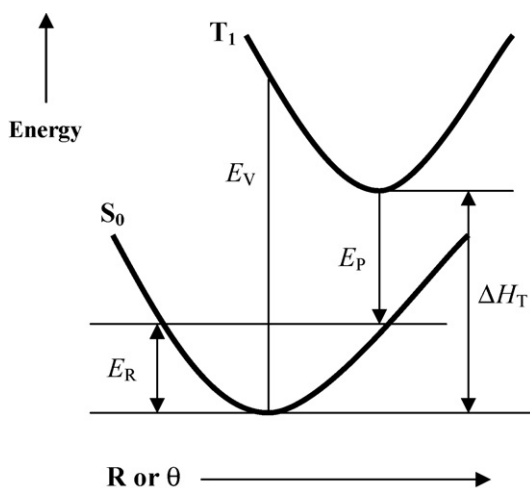


Fig. 6. Representative potential energy relationships between T_1 and S_0 vs. a critical coordinate, R or θ .

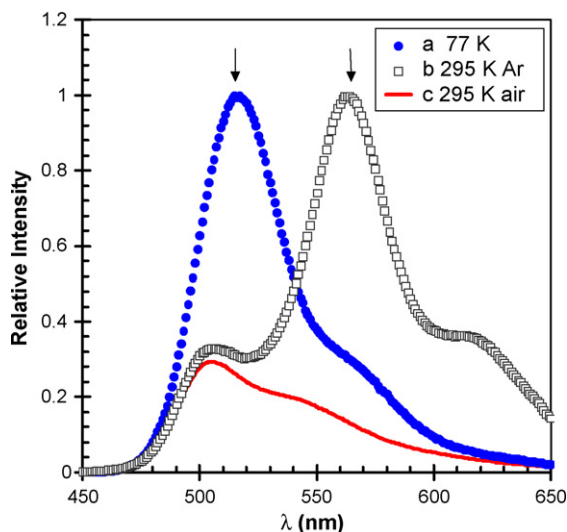


Fig. 8. Emission spectra of 5 mM benzil in (a) ethyl acetate at 77 K, (b) argon-purged ethyl acetate at 295 K and (c) air-saturated ethyl acetate at 295 K, all excited at 400 nm.

cyclohexane at 293 K [32]. The weaker hypsochromic band in the argon-purged solution at 295 K is due to fluorescence. As shown in (c), only this fluorescence remains in an air-saturated solution due to efficient quenching of benzil triplets. (The 1600 cm^{-1} spacing between the 0,0 phosphorescence band and the 0,1 band in (b) corresponds to the carbonyl stretching frequency of the dominant vibrational progression. For insight into how dominant vibronic transitions relate to the overall potential energy surfaces see Fig. 1 of Ref. [33].)

The difference between the 295 K and the 77 K benzil phosphorescence maxima of 4.6 kcal/mol is remarkably large and similar to the ($E_T - E_P$) difference. Even allowing for the bathochromic shift in the 77 K phosphorescence at longer excitation wavelengths, the difference between the 295 K and the 77 K phosphorescence energies will be ≥ 3.6 kcal/mol. Assuming minimal T_1 relaxation at 77 K, the phosphorescence maximum in frozen ethyl acetate will correspond approximately to E_V in Fig. 6. The value of E_R in Fig. 6 depends on the shapes of the potential energy surfaces. If the T_1 and S_0 surfaces have similar parabolic shapes, then $E_R \sim 1/2 (E_V - E_P)$ or about 1.8–2.3 kcal/mol. With these assumptions, about half of the ($E_T - E_P$) difference of 4.3 kcal/mol for benzil would arise from E_R and about half from ΔS_T .

The temperature dependence of the phosphorescence of 2,2'-diethoxybenzil (DEB) is even greater than that of its benzil parent. The excitation wavelength-dependent phosphorescence energy of DEB at 77 K is 60.7 ± 0.9 kcal/mol, while the excitation wavelength-independent E_P at 295 K is 50.9 kcal/mol, similar to the value of ~ 51 kcal/mol reported in cyclohexane at 293 K [32]. (A similar temperature effect has been noted for *o*-anisil phosphorescence [34].) The very large decrease in E_P for DEB from 77 K to 295 K implies a large E_R (Fig. 6). This E_R is probably a major contributor to the large ($E_T - E_P$) difference of 8.0 kcal/mol (Table 1) for DEB at 295 K.

It is interesting to note that for many of the molecules for which E_T is substantially greater than E_P , the phosphorescence

energies at 77 K are reasonably close to the E_T values. Because of this, the use of low-temperature phosphorescence data to assign triplet energies in solution at ambient temperature for nonrigid molecules, while unadvisable, tends to yield values that are often not too far in error. For example, for the ketocoumarins the low-temperature phosphorescence energies [16] are typically within about 0.3 kcal/mol of the E_T values in Table 1, even though the E_P values are about 1–1.5 kcal/mol less than the E_T values. Similarly for the benzil and DEB, the phosphorescence energies at 77 K are relatively close to the E_T values. For the polyphenyls the 77 K phosphorescence energies are between E_T and E_P . This similarity arises because the increased emission energies from unrelaxed T_1 configurations at 77 K tend to offset the positive $-T\Delta S_T$ contributions to E_T from the decreased T_1 entropies of these nonrigid molecules.

5. Conclusions

Thermodynamic triplet free energies, E_T , referenced to an E_T of 60.5 kcal/mol for naphthalene, have been provided for 23 donor/sensitizers and 37 acceptors in ethyl acetate at 295 K. The E_T measurements in solution involve equilibrated energy transfer over time scales sufficient for molecular (solute and solvent) relaxation. Thus they provide energy differences between T_1 molecules in their most stable equilibrium nuclear configuration and S_0 molecules in their most stable nuclear configuration, and reflect contributions of both enthalpy and entropy differences between T_1 and S_0 . These E_T values offer a reliable basis set of triplet energies for quantifying both the kinetics and the efficiencies of energy transfer processes in solution.

Phosphorescence energies, E_P , at 295 K were also measured for most of the donors and many of the acceptors. While E_T and E_P values tend to be quite similar for rigid chromophores (e.g., xanthenes, thioxanthenes, naphthalenes and phenanthrenes), E_T values are substantially greater than E_P values for chromophores with configurational freedom (e.g., ketocoumarins, α -diketones and polyphenyls). The larger E_T values include contributions from (a) $-T\Delta S_T$ due to the decreased entropy of the more conjugated T_1 states and (b) the S_0 relaxation enthalpy, E_R , reflecting the fact that E_P involves a vertical transition from T_1 to S_0 in the T_1 geometry, whereas E_T reflects the enthalpy difference between T_1 and S_0 , each in its equilibrium geometry. The former contribution appears to predominate for the polyphenyls. Interestingly, E_P triplet energies for nonrigid chromophores obtained from low-temperature phosphorescence measurements are often similar to E_T values at 295 K even though the former do not include the substantial entropy differences between T_1 and S_0 . This similarity arises because the increases in the E_P transition energies due to incomplete T_1 relaxation in the former case tend to be of similar magnitude to the positive ΔS_T contributions to E_T values.

Donor triplet quantum yields are provided, which hopefully will prove useful for sensitization experiments. T–T absorption maxima and ϵ values are also provided for all 60 donors and acceptors.

Acknowledgements

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jphotochem.2007.06.014.

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