Distortion of the Fluorescence Spectrum of *all-trans*-1,6-Diphenyl-1,3,5-hexatriene with Increasing Laser Pulse Excitation Energies

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At high laser pulse excitation energies the fluorescence spectrum of *all-trans*-1,6-diphenyl-1,3,5-hexatriene, DPH, undergoes distortion that can be modeled as the development of a new broad fluorescence, $\lambda_{max} = 497$ nm, which builds up biphotonically with increasing excitation laser pulse power. This phenomenon is observed upon excitation at either 266 or 355 nm in a variety of organic solvents, provided [DPH] and excitation intensity are sufficiently high. Four possible sources for the distortion of the fluorescence spectrum are investigated: (1) excimer emission arising from DPH radical cation/anion pairs, (2) bicimer fluorescence from the encounter of two S_1 states, (3) $S_n \rightarrow S_1$ fluorescence, and (4) self-absorption due to overlap of the fluorescence with transient absorption spectra. The first three possibilities are ruled out. The fourth is viable, revealing an effective transient absorption spectrum that agrees well with the known $S_n \leftarrow S_1$ absorption spectrum at long wavelengths.

Introduction

High laser excitation energies can elicit spectroscopic responses that cannot be explained by the photophysics of a single molecule because they involve the response of two or more molecules. A prominent example of nonlinear collective molecular response is the appearance of multiple amplified spontaneous emission (ASE) laser spikes from solutions of benzoxazole derivatives subjected to highly intense laser excitation.[1,2] These multi-ASE spikes have been attributed to a new class of concealed excited state conformers, the electromers. This study of *all-trans*-1,6-diphenyl-1,3,5-hexatriene (DPH) was undertaken because it exhibits complex fluorescence reflecting both excited-state equilibration and ground-state conformer equilibration that could provide alternative mechanisms for the origin of multi-ASE laser spikes.

The molecule DPH possesses large molecular absorptivity values[3] and high fluorescence quantum yields, especially in hydrocarbon solvents,[4] and has received attention in studies of nonlinear optical properties.[5] The complex fluorescence behavior of this molecule is very well understood. In contrast to the first two members of the α,ω-diphenylpolyene family whose fluorescence in solution originates from the 1^1B_u state, the lowest single-photon-allowed excited singlet state, the bulk of DPH fluorescence was assigned by Hudson and Kohler to the one-photon-forbidden but two-photon-allowed $2^1A_g \rightarrow 1^1A_g$ transition.[6,7] Although strongly symmetry-forbidden and not readily observable in the single-photon absorption spectrum of DPH, the $2^1A_g \leftarrow 1^1A_g$ transition is observed in the two-photon absorption (fluorescence excitation) spectrum.[8] It is also active in the fluorescence spectrum because of vibronic coupling between the 2^1A_g and the nearby 1^1B_u state.[9,10] The extent of this mixing is strongly dependent on the energy gap, ΔE_{ba}, which is highly sensitive to the polarizability of the medium.[6,9] Decay of the initially formed 1^1B_u state to an equilibrium mixture of two $2^1A_g/1^1B_u$ mixed states, the higher mainly 1^1B_u and the

lower mainly 2^1A_g in which the latter is dominant, is complete in the subpicosecond time scale.[11–13] The $1^1B_u \rightarrow 1^1A_g$ transition is observed as a solvent and temperature dependent weak shoulder at the onset of the DPH fluorescence spectrum.[9,10,14] This dual fluorescence is due to excitation of the thermodynamically favored s-trans ground state conformer of DPH.[15] Excitation of an s-cis conformer, whose population is small at ambient temperature, yields a third fluorescence spectrum that is redshifted with respect to the other two and whose contribution is enhanced upon excitation at the onset of the DPH absorption spectrum.[15]

Transient absorption spectra of the radical cation and anion of DPH in solution were reported first by Almgren and Thomas.[16] In cyclohexane, both species form on pulse radiolysis (λ_{max} at 635 and 660 nm, respectively), but neither is observed on pulsed laser photoexcitation. Formation of the radical cation occurs by two-photon photoionization in ethanol, dichloroethane, and various micelles.[16] In agreement with these observations, Wang and McGimpsey reported two-photon generation of the radical cation (DPH•+, 590 nm) in acetonitrile solution and its absence in cyclohexane.[17] A strong solvent dependence of the efficiency of DPH photoionization to yield DPH radical cations and radical anions was also revealed by time-resolved resonance coherent anti-Stokes Raman scattering measurements.[18]

In this paper we describe the excitation pulse intensity dependence of the luminescence response of DPH at 298 K in methylcyclohexane (MCH) and acetonitrile (AN). Effects of O_2 and fumaronitrile on the DPH spectra aid the interpretation of our observations. Similar behavior is reported for a rigid analogue of DPH.

Experimental Section

DPH from Aldrich, 98% purity, was chromatographed on silica gel with ethyl acetate/petroleum ether (1:99 v/v) as eluent and then twice recrystallized from *n*-hexane (Aldrich, Spectrophotometric grade). *all-trans*-Diindanylidenyl-2-butene (*stiff-5*-DPH) was as previously described.[19] Petroleum ether (Baker,

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reagent grade) was distilled prior to use. The solvents used were spectrophotometric grade.

All spectroscopic observations were made in solution at 298 K for the concentrations and solvents given in the text and the figure legends. The emission spectra were recorded, as previously described for ASE measurements,[1] by primary excitation with a Nd:YAG laser (Spectra-Physics Quanta-Ray DCR-3G), using the second (532 nm), third (354 nm), and the fourth (266 nm) harmonics. Laser pulse repetition was 10 Hz and the pulse duration was 5 ± 1 ns. The output of the Nd:YAG laser was focused to a narrow line horizontally across the dye cell (the cylindrical lens focus distance was 16 cm, and the cell was placed $11-12$ cm from the lens). A Molectron DL 251 laser dye cell of 0.8 cm optical length was used, with oblique windows designed to prevent optical feedback from the windows. The dye solution was stirred to minimize secondary processes (local heating, triplet population, etc.) from interfering with the experiments. The sample emissions were dispersed by a 300 lines/mm and 0.32 m polychromator (Instruments SA model HR320), detected by an optical multichannel analyzer (EG&G/PAR, model 1421) and analyzed by a system processor (EG&G/PAR, model 1461/1463). To reduce the noise, the detector was operated in a gated-mode synchronously with the Nd:YAG laser. The intensities of the primary laser excitation were optically calibrated with a volume-absorbing disk calorimeter (Scientech, Inc., model 36-0001). Emission spectra are uncorrected for instrumental nonlinearity. Solutions were freshly prepared at the concentrations indicated in the figure legends. Photostability of the compounds studied was demonstrated by monitoring the absorption spectra before and after the laser experiments, using a cuvette of 0.01 cm optical length. The absorption spectra (not shown) were recorded by use of a Shimadzu UV-2100 spectrophotometer. Photoinstability was negligible during the experimental time. Some of the methyl-cyclohexane solutions of DPH were Ar- or oxygen-outgassed, using a prebubbler to avoid loss of solvent. Some samples of DPH were degassed with a vacuum system to 3.5×10^{-5} Torr using five freeze/pump/thaw cycles. Principal component analyses with self-modeling (PCA-SM) calculations were performed on a limited Dell DIMENSION PC with a Pentium processor using FORTRAN language as previously described.[20]

Results and Discussion

Concentration and Excitation Intensity Dependencies. As can be seen in Figure 1a, the fluorescence spectrum of DPH, 2.4×10^{-3} M, in Ar-outgassed methylcyclohexane (MCH) appears to develop a new emission band with an apparent λ_{max} at approximately 490 nm that gains in relative intensity as the pumping laser pulse intensity at 354 nm is increased from 0.23 to 13.6 mJ/pulse. The phenomenon is reversible and not a result of permanent photochemical changes as this new band disappears with diminishing pumping intensity. Furthermore, the initial DPH fluorescence at low excitation intensity is identical to the final fluorescence spectrum at the end of this experiment (both measured with 0.23 mJ/pulse) and no significant differences are detected between initial and final absorption spectra. The spectral profiles of DPH fluorescence for the lowest (0.23 mJ/pulse) and the highest (13.6 mJ/pulse) laser excitation intensities are compared in Figure 1b. The same luminescence behavior is also observed when a 2.4×10^{-3} M DPH in O_2-saturated MCH solution is employed. The presence of O_2 diminishes fluorescence intensity 4-fold without affecting the shapes of the fluorescence spectra. No change in the fluorescence spectrum of a 2.2×10^{-5} M DPH solution is observed,
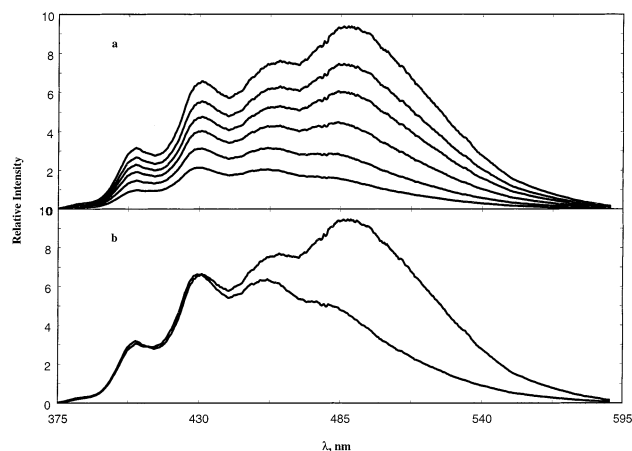
Figure 1. (a) Fluorescence spectra of *ttt*-DPH, 2.4×10^{-3} M, in Ar-outgassed MCH as the excitation laser pulse intensity (354 nm) is increased in the order 0.23, 1.11, 2.62, 5.20, 7.96, and 13.65 mJ/pulse. (b) Comparison of spectral profiles for the lowest (0.23 mJ/pulse) and highest (13.65 mJ/pulse) laser excitation intensities.

even on exciting with 27.5 mJ/pulse. The dependencies of these spectral changes on ground-state concentration and on pumping excitation intensity suggest multimolecular and multiphotonic origins. Pronounced changes in the fluorescence spectrum profile are observed only when thresholds of high ground-state concentration and high pumping intensity are attained. Similar changes are observed upon excitation at 266 nm and on changing the solvent to dioxane or acetonitrile. Identical fluorescence spectra are obtained using either circularly or linearly polarized laser excitation pulses.

PCA-SM Procedure. Since detailed descriptions of the PCA-SM curve resolution procedure are available,[20] only a brief summary is provided here for the convenience of the reader. The rows of the input spectral matrix are normalized (sum of elements of each row is unity) spectra, S_i. The PCA mathematical procedure gives a set of eigenvalues and a corresponding set of eigenvectors (also known as abstract spectral vectors) from which the number of components is inferred on the basis of the relative magnitude of the eigenvalues and the shapes of the eigenvectors. For a two-component system the experimental spectra can be represented as a linear combination of the two eigenvectors V_α and V_β corresponding to the two largest eigenvalues.

$$S_i = \alpha_i V_\alpha + \beta_i V_\beta \tag{1}$$

Combination coefficients (α_i, β_i) of the ith spectrum are obtained from dot products of the spectrum with each eigenvector (e.g., $\alpha_i = S_i \cdot V_\alpha$) because the eigenvectors are orthonormal. Since the sum of the elements in S_i is unity,

$$\alpha \sum_{j=1}^{n} v_{\alpha j} + \beta \sum_{j=1}^{n} v_{\beta j} = 1 \tag{2}$$

eq 1 requires that the eigenvectors define a normalization line in α, β space on which combination coefficients (α_i, β_i) of all spectra that are combinations of the two pure component spectra must fall. Determination of the combination coefficients (α_A, β_A) and (α_B, β_B) of the pure component spectra S_A and S_B on the normalization line is the task of the SM procedure. When the two pure spectra are displaced with respect to each other on the wavelength scale, SM, based on the Lawton and Sylvestre constraint that S_A and S_B have no negative elements, suffices in defining essentially unique combination coefficients for the

two spectra.[20] Once the length of the normalization line from (α_A, β_A) to (α_B, β_B) is determined, the fractional contributions, x_{Ai} and x_{Bi}, of the pure spectra, S_A and S_B, to each experimental spectrum S_i are defined by the location of (α_i, β_i) on the normalization line on the basis of the lever rule.[20]

Resolution of Excimer-like Emission. Principal component analysis (PCA) was carried out separately on the emission spectra obtained for 2.4×10^{-3} M DPH in Ar- or O$_2$-saturated MCH.[20] Each matrix behaves as a multicomponent system when all emission spectra are included in each treatment. Inspection of the spectra reveals more sharply defined vibronic structure in the monomer portion of the emission spectra at the higher laser excitation powers, obvious at the onset in Figure 1b. Two possible sources of nonlinear spectral changes were readily eliminated: (i) formation of *ctt*- and *tct*-DPH by photoisomerization of DPH;[21] (ii) variable self-absorption due to increased ground-state depletion with increasing laser power. Although DPH photoisomerization to the cis isomers is known to occur with low quantum yields in MCH,[21] its contribution was negligible, as evidenced by identical emission spectra obtained for low laser excitation intensity at the beginning and at the end of each experiment. That the nonlinear changes in the DPH fluorescence spectra are most pronounced at the lowest laser excitation intensities was demonstrated by progressively removing low-intensity spectra from each data set and repeating the PCA treatments. Robust two-component systems resulted when emission for the three lowest excitation intensities were eliminated from each matrix. The PCA treatment was repeated on truncated matrices, confined to the 415−591 nm range, which should be unaffected by $S_2 \leftarrow S_0$ DPH self-absorption. No improvement in eigenvalue ratios was obtained, indicating that variable self-absorption does not contribute significantly to the nonlinear changes when the entire 361−591 nm range is employed.

The spectrum of the supposed new component, a structureless excimer-like emission, was obtained by imposing the self-modeling (SM) constraint of baseline in the 361−415 nm region. Although the two matrices yield nearly identical spectra, the spectrum obtained from the matrix of the spectra for the O$_2$-saturated solution is blue-shifted by ∼4 nm. The corresponding monomer spectra are not shifted with respect to each other. Application of PCA-SM on a global matrix consisting of the spectra from the Ar- and O$_2$-saturated solutions together with the average excimer-like emission from the separate treatments reveals a two-component system to a very good approximation. The derived pure-component spectra are shown in Figure 2. The principal eigenvector from the PCA treatment of the low-concentration DPH spectra, which are independent of laser power and comprise a one-component system, is shown in Figure 2 for comparison. It can be seen that the monomer spectrum derived from the treatment of the high [DPH] spectra shows better definition of vibronic structure and returns more rapidly to baseline at longer wavelengths.

The near-identity of the onsets of the low and high [DPH] monomer fluorescence spectra in Figure 2 suggests that these measurements are not affected by ground-state self-absorption. This may seem surprising in view of the very high absorbance at the 355 nm excitation wavelength under the conditions used to obtain the spectra in Figure 1. However, it is this high absorbance that ensures that the detected fluorescence originates very close to the front face of the cell and, consequently, is not significantly self-absorbed. When 266 nm excitation laser pulses are employed on solutions of the same high concentration, the
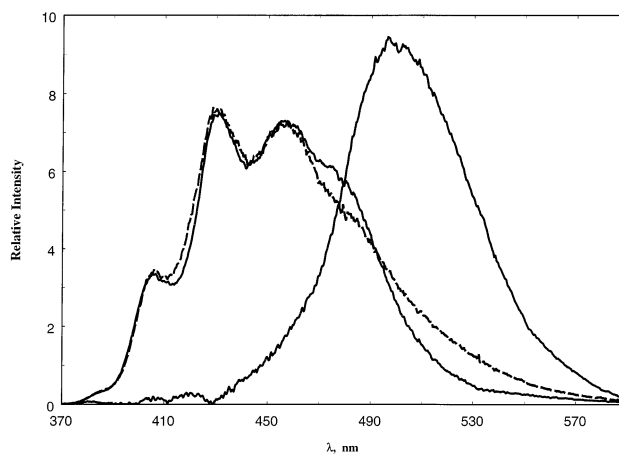
Figure 2. PCA-SM resolved monomer and excimer-like *ttt*-DPH fluorescence spectra from a global matrix containing spectra for Ar- and O$_2$-outgassed MCH in a single matrix (solid lines) compared with the principal eigenvector of the low concentration *ttt*-DPH (2.2×10^{-5} M in Ar-outgassed MCH) spectra over the same pulse excitation intensity range (dashed line).

much lower absorbance of the sample allows much deeper penetration by the exciting beam and the fluorescence spectra show the expected self-absorption at the onset.

Apparent Biphotonic Origin of the New Emission. The spectral behavior in Figure 1 is reminiscent of earlier observations that have been attributed to the development of bicimer emission at high laser excitation energies due to intramolecular[22] or intermolecular[23] interaction between two singlet excited chromophores. Specifically, bicimer[22] formation has been postulated in push−pull disubstituted diphenylpolyenes **1** ($n = 1-3$).[23] Bicimer fluorescence appears at the red edge of the


1 ($n = 1-3$)
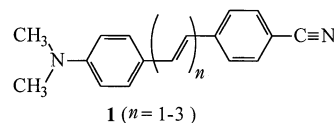
normal fluorescence at high solute concentrations and high laser intensities. The involvement of two S$_1$ molecules in bicimer formation requires that such emissions be biphotonic as has been established for the stilbene member of the series **1** ($n = 1$).[23a]

A higher order excitation energy dependence for the excimer-like emission is an implicit assumption of the spectral resolution in the preceding section. Since the area of monomer emission (A_m) should be proportional to the effective concentration of excited singlets of DPH, the bicimer mechanism requires that the slope of the plot of log A_e vs log A_m, where A_e is the area of the excimer-like emission, be equal to 2. The slope of the log−log plot of the resolved areas (Figure 3) is 2.0 ± 0.1, seemingly confirming this expectation. However, the bicimer mechanism also requires that separate plots of log A_e and log A_m vs log I_{exc}, where I_{exc} is the excitation laser pulse power, should be linear with maximum slopes of 2 and 1, respectively. Actually, although linear, the slopes of these plots (not shown) are 0.6 and 0.3, respectively, revealing that the emissions are strongly attenuated. Another difference between bicimer emissions and the excimer-like emission that seems to develop in DPH is that bicimer emissions from **1** ($n = 1-3$) are only observed in polar solvents, where evidence, based on structurally restricted analogues, suggests that a TICT state involving twisting of the dimethylanilinium moiety is an essential precursor.[23] In contrast, identical behavior is observed for DPH and from *stiff-5*-DPH, independent of the polarity of the solvent.

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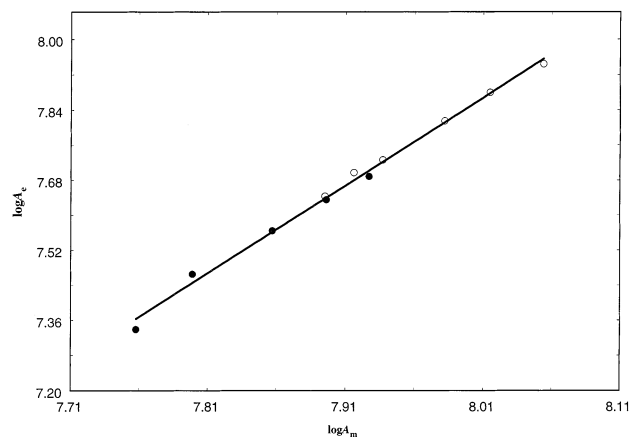
Figure 3. Logarithmic plots of the area of the excimer-like emission vs the area of the monomer emission: Ar-outgassed spectra (○); O_2-outgassed spectra (●). The slope of the line is exactly 2.0.

stiff-5-DPH
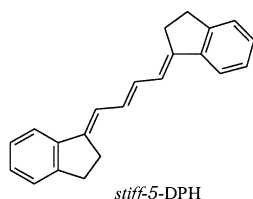
An even more compelling reason for rejecting the bicimer mechanism as an explanation for the changes in the DPH fluorescence spectra is that these changes are not significantly affected by the presence of O_2. This is evident in Figure 3 where points corresponding to spectra for Ar- and O_2-saturated solutions fall on the same line. Substitution of O_2 for Ar in solutions of DPH in MCH at 30 °C attenuates the fluorescence intensity by a factor of 4.3 under conventional fluorimetric conditions of very low concentration and excitation intensity.[24] Consistent with the slightly lower temperature, a ratio of 4 is obtained in this work, independent of laser excitation power. Since bicimer formation involves a bimolecular encounter between two S_1 states, a factor of 16 quenching of the excimer-like emission was expected, and this is clearly not the case.

Since formation of DPH radical cations is known to be biphotonic,[16,17] it is tempting to seek an explanation that connects the two phenomena. A possible scenario would involve photoionization of S_1 DPH with the second photon and capture of the ejected electron by a ground-state DPH molecule.[18] An encounter between radical cation and radical anion DPH molecules, formed in proximity, could generate an excimer and account for the structureless new emission. The alternative of ground-state association of DPH molecules is not likely because the DPH absorption spectrum is independent of concentration in MCH for the entire concentration range employed in these measurements.

Spooner and Whitten observed fluorescence from DPH aggregates from molecules having the DPH moiety covalently embedded in the backbone of a fatty acid, $_4H_4A$.[7b,25] A
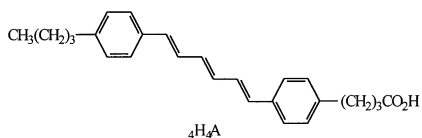
$_4H_4A$

multilayer Langmuir−Blodgett assembly composed of a 1:1 mixture of $_4H_4A$ with arachidic acid, AA, shows an excitonic type absorption spectrum and a broad structureless excimer-

like fluorescence spectrum.[25] These aggregate spectra are replaced by monomer spectra, similar to those of $_4H_4A$ in dilute solution when a 1:20 $_4H_4A$/AA mixture is employed. The $_4H_4A$ aggregate emission is much broader than the excimer-like fluorescence derived in this work, but the λ_{max}s of the two spectra are nearly coincident.

Tests of the Excimer Mechanism. The excimer mechanism seemed doubtful at the outset. The absence of excimer formation by the normal pathway of S_1/S_0 DPH interaction and the absence of biphotonic $^2DPH^{•+}$ formation in hydrocarbon solvents,[16,17] under conditions that readily give rise to this transient in acetonitrile, might be rationalized by the requirement of sufficiently high DPH concentration to allow capture of the ejected electron from S_1 by a nearby S_0 molecule. However, DPH radical ion pairs, formed in this way in AN, would separate to give free radical ions, and significant quenching of excimer emission in that solvent would be expected. Also, DPH radical anions are quenched preferentially by oxygen in AN,[18] but the fluorescence behavior of DPH in AN is very similar to that in MCH. Furthermore, the $\lambda_{max} = 489 \pm 1$ nm of the analogously derived emission in AN is blue-shifted relative to MCH and does not reveal the stabilization expected for a contact radical ion pair in the more polar solvent.

The radical ion pair mechanism was further tested by repeating the measurements in MCH in the presence of fumaronitrile (FN), [DPH] $= 2.2 \times 10^{-3}$ M, [FN] $= 5.4 \times 10^{-3}$ M. FN is an excellent electron acceptor that is known to quench $^1DPH^*$ at nearly diffusion-controlled rates in both polar and nonpolar solvents.[26−29] If the electron ejection step in eq 3 were playing a role in the development of the 497 nm emission, then competitive capture of ejected electrons by FN would diminish the intensity of this emission. No such quenching was observed.

Transient $S_n \leftarrow S_1$ Self-Absorption as the Source of the Phenomenon. As stated in the Introduction, the lowest excited DPH singlet state formed on single-photon absorption is S_2.[6,7] The S_2/S_1 equilibrium mixture[14] attained in the femtosecond time scale strongly favors S_1.[11−13] Vibronic coupling between the 2^1A_g and 1^1B_u states of DPH[9,10] gives rise to these mixed excited singlet states with S_1 and S_2 being primarily 2^1A_g and 1^1B_u in character, respectively. The equilibrium population of S_2 is evident in the fluorescence spectrum,[14] but its contribution in the transient singlet−singlet absorption spectrum is negligible.[11] Accordingly, DPH transient singlet−singlet absorption spectra can be assigned entirely to $S_n \leftarrow S_1$ transitions.[11] Reported spectra in MCH consist of two broad bands with λ_{max} at 460 and 650 nm, respectively, and a shoulder at 700 nm.[11,30] Of these, the "460 nm band" is the most intense and its strong overlap with the DPH fluorescence spectrum probably accounts for the absence of ASE action. Triplet−triplet absorption extends from 350 to 440 nm with $\lambda_{max} = 416$ nm in cyclohexane, but the intersystem crossing quantum yield, $\phi_{is} = 0.03$, is small.[31] No interference by the DPH radical cation is expected, since its absorption was not detected in cyclohexane and in polar solvents it absorbs[16,17] well to the red of the fluorescence. The location of the 460 nm $S_n \leftarrow S_1$ band also raises the possibility that the 497 nm emission corresponds to $S_n \rightarrow S_1$ fluorescence, but this possibility is ruled out because the fluorescence spectrum observed at low DPH concentration is not excitation pulse energy dependent.

Significant absorption of the fluorescence of DPH by the excited singlet transient could distort the fluorescence spectrum, the distortion increasing progressively with increasing laser power. The appearance of enhanced intensity at longer wave-

lengths could then be due to preferential transient absorption at the onset of the DPH fluorescence spectrum. Quantitative determination of the effect of the 460 nm $S_n \leftarrow S_1$ DPH absorption band on DPH fluorescence requires an accurate absorption profile for this band. This absorption band, or parts thereof, has been measured independently in four different investigations.[11,30] Agreement is reasonable for the long wavelength onset of this absorption, but there is considerable uncertainty as to its shape at shorter wavelengths. Two lower resolution point-by-point spectra, which were obtained by employing nanosecond excitation pulses, place the λ_{max} at 450 nm and show diminution in absorptivity by about a factor of 2 at 400 nm.[30a,b] Two higher resolution spectra, for which picosecond excitation pulses were employed, place the λ_{max} at 460 nm,[11,30c] but only one of these extends to 400 nm where it shows a complete return to the baseline.[30c] The low intensities of the picosecond probe pulses at wavelengths close to 400 nm render the accuracy of measurements in that wavelength region questionable. Initially, the partial spectrum in ref 11 was extended to shorter wavelengths by assuming symmetry[30c] about 460 nm. This spectrum was used to create a simulated spectral matrix by applying it as a filter on the lowest excitation power spectrum in Figure 1. Changes in the DPH fluorescence spectrum profile were achieved by stepwise increase of the absorbance at 460 nm (0.01 absorbance increments) in the 0.01–0.10 absorbance range. PCA-SM treatment of the simulated spectra revealed an excellent two-component system. However, since the filtering effect is most pronounced in the center of the fluorescence spectrum, the analysis returns a hypothetical pure-component spectrum (Lawton and Sylvestre limit[20]) that resembles that of DPH with its central part removed. We were encouraged, however, because the low-energy part of this spectrum is very similar to the pure-component excimer-like spectrum in Figure 2.

In a second attempt, we relied on the $S_n \leftarrow S_1$ spectrum of Das and co-workers, which extends furthest into the UV region.[30b] It was used to extend the absorption spectrum in ref 11, and with this composite absorption spectrum the simulation process was repeated. Again, a PCA-SM "pure-component" spectrum was derived whose low-energy profile resembles closely the excimer-like spectrum in Figure 2. Although considerably attenuated, the spectrum still exhibits residual emission in the 370–410 nm region where the baseline is nearly attained in the excimer-like spectra derived from the experimental observations.

The partial success of the above simulations strongly suggests $S_n \leftarrow S_1$ self-absorption as the major source of the distortion of the DPH fluorescence spectra. Discrepancies in the spectra derived from the above simulations in the 370–410 nm region could reflect underestimation of $S_n \leftarrow S_1$ absorbance in the determinations of this transient absorption spectrum in that region, or, less likely, the build-up of other unknown transients. To derive the transmittance spectrum that converts the spectrum for the lowest excitation intensity and lowest concentration to the shape observed for the highest excitation intensity in Figure 1a, the high excitation intensity spectrum was attenuated to achieve coincidence of the two spectra at 535 nm where there is no $S_n \leftarrow S_1$ absorbance.[11,30] The transmittance spectrum was then calculated as the product of the inverse of the low-intensity, low-concentration spectrum and the attenuated high-intensity spectrum. Converted to absorbance, this spectrum is shown in Figure 4. With the use of this spectrum the experimental spectra in Figure 1a are reproduced nearly exactly from the lowest intensity spectrum by varying its effective absorbance at 420
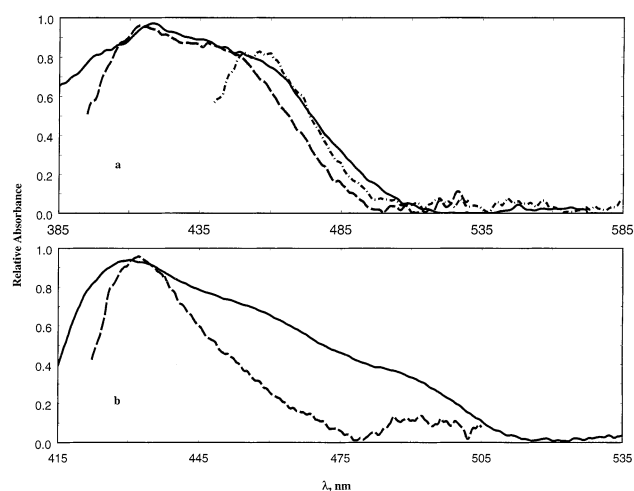
Figure 4. Effective $S_n \leftarrow S_1$ absorption spectra of (a) DPH and (b) *stiff*-5-DPH in MCH (1.0×10^{-3} M, —) and in AN (2.4×10^{-3} M, - - -). Also shown is the transient DPH absorption spectrum in MCH (-•-) from ref 11.

nm, as required, in the range 0–0.63 AU. Even the small apparent shift in the excimer-like emission spectrum obtained from the separate analysis of spectra for the O_2-saturated solutions is reproduced because, due to S_1 quenching by O_2, the effective S_1 absorbances achieved in the presence of O_2 are lower. Inclusion of all the calculated spectra in the PCA-SM matrix also reproduces the multicomponent behavior noted in the analogous treatment of the experimental spectra. The value of the slope of the line in Figure 3 also makes sense. Partial attenuation of the fluorescence spectrum requires a second photon that produces the interfering transient absorption. The resolution achieved by PCA-SM approximately separates the self-absorbed portion of each spectrum from the portion that experiences no self-absorption (the excimer-like spectrum). This accounts for the 2:1 excitation power dependence because the expected relationship is roughly 1:0.5. The observed slopes of 0.6 and 0.3 of plots of log A_e and log A_m vs log I_{exc} reveal the very strong influence of self-absorption.

We conclude that the laser excitation power dependence of the fluorescence of DPH is due primarily to self-absorption. The S_1 excited state of DPH absorbs its own fluorescence, thereby distorting the fluorescence spectrum. Correcting for this distortion reveals an effective transient absorption spectrum in the 385–585 nm region (Figure 4) that is in good agreement with direct measurements of the $S_n \leftarrow S_1$ absorption in the 450–530 nm region.[11,30] The $S_n \leftarrow S_1$ absorption spectrum in MCH from ref 11 is included in Figure 4 for comparison. Discrepancies at shorter wavelengths may be attributed to the combined effects of inaccessibility of this wavelength region to the picosecond measurements and, more generally, to difficulties in correcting the spectra for fluorescence interference and ground-state depletion. The above procedure also yields effective transient absorption spectra for DPH in AN and for *stiff-5*-DPH in MCH and in AN (Figure 4).

Concluding Remarks

The appearance of the DPH fluorescence spectrum is strongly dependent on laser excitation power. The changes could be modeled quantitatively as the build-up of a broad, structureless, excimer-like fluorescence band centered at 497 nm. In pursuit of this illusion, a strictly biphotonic excitation power dependence for the appearance of this band was established that led to the investigation of excimer and bicimer mechanisms for the

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observed changes. The exercise of excluding these mechanisms is presented here because of its instructive value and to show how easily one can be misled. The origin of the spectral distortions is traced, at least in part, to $S_n \leftarrow S_1$ self-absorption, and on this conclusion, accurate $S_n \leftarrow S_1$ absorption spectra are derived for DPH and *stiff-5*-DPH in MCH and AN. Effective transient absorption spectra, whose direct measurement is hampered by concomitant fluorescence and ground-state bleaching, are obtained here by quantitative analysis of the distortion of the fluorescence spectrum at high excitation intensities.

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