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# Fluorescence Spectral Patterns of $\alpha,\omega$-Diphenylpolyenes near the $S_1(2^1A_g)$ and $S_2(1^1B_u)$ Level Crossing Point in Solution

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The changes of the fluorescence spectral patterns observed when the $S_2(1^1B_u)$ level is approached the $S_1(2^1A_g)$ level by varying the solvent polarizability have been investigated for *all-trans*-1,6-diphenyl-1,3,5-hexatriene (DPH) and *all-trans*-1,8-diphenyl-1,3,5,7-octatetraene (DPO) in room temperature solvents. It is shown that the emission of DPO in diiodomethane consists nearly of a 1 : 1 mixture of the $S_2$ and $S_1$ fluorescence and that the emission of DPH in $CS_2$ consists almost entirely of the $S_2(1^1B_u)$ fluorescence. When the $1^1B_u$ level approaches the $2^1A_g$ level, not only the increase of the $S_2$ fluorescence intensity but also the change in the spectral pattern of the $S_1$ fluorescence are observed for DPH and DPO. The solvent polarizability that achieves the inversion of the $2^1A_g$ and $1^1B_u$ levels for DPO has been estimated to be 0.54.

The discovery of an excited state $^1A_g$ below the strongly allowed $^1B_u$ state of polyenes not only forced a fundamental revision of the accepted molecular orbital picture of polyene electronic structure, but also explained properties of polyenes that had been termed anomalous.[1–4] Normally the existence of the lowest excited $2^1A_g$ state of polyenes cannot be confirmed in the optical absorption spectra, because of the extremely weak transition intensities and of the masking effect due to the strong $S_0(1^1A_g) \rightarrow S_2(1^1B_u)$ absorption. However, it is possible to obtain some spectral features which indicate the existence of the $2^1A_g$ state located at energies lower than the $1^1B_u$ state through the emission measurements. For example, the location of the $2^1A_g$ fluorescence is almost unchanged, while the $1^1B_u$ absorption shifts with varying the solvent polarizability for $\alpha$, $\omega$-diphenylpolyenes.[4,5] Further, for both 1,6-diphenyl-1,3,5-hexatriene (DPH) and 1,8-diphenyl-1,3,5,7-octatetraene (DPO), the weak $S_2(1^1B_u)$ fluorescence is observed at the blue shoulder of the strong $S_1(2^1A_g)$ fluorescence.[6–10]

In a foregoing paper we have demonstrated that, in a sufficiently polarizable solvent, it is possible to invert the $2^1A_g$ and $1^1B_u$ levels of DPH.[11] We have recently shown the fluorescence spectral change observed when the $1^1B_u$ level approaches the $2^1A_g$ level for 1,4-diphenyl-1,3-butadiene.[12] By varying the solvent polarizability so as to bring the $2^1A_g$ level close to the $1^1B_u$ level, interesting spectral changes are expected to be observed also for DPH and DPO due to the strong vibronic coupling between the $2^1A_g$ and $1^1B_u$ states.[13] Further, $\alpha$, $\omega$-diphenylpolyenes, in particular DPH and DPO, are often used as fluorescence probes. Thus, we have investigated the change of the fluorescence spectral patterns observed when the $1^1B_u$ level approaches the $2^1A_g$ level for DPH and DPO. It is shown that the emission of DPO in diiodomethane consists nearly of a 1:1 mixture of the $S_1(2^1A_g)$ and $S_2(1^1B_u)$ fluorescence and that the emission of DPH in $CS_2$ consists almost entirely of the $S_2(1^1B_u)$ fluorescence. The changes of the spectral pattern of the $S_1(2^1A_g)$ fluorescence that occur with decreasing the $1^1B_u$–$2^1A_g$ energy separation have been analyzed quantitatively for DPH and DPO in solution.

## Experimental

1,6-Diphenyl-1,3,5-hexatriene (DPH) and 1,8-diphenyl-1,3,5,7-octatetraene (DPO) used in the present experiment were obtained from Aldrich Chemical Co., USA, and were recrystallized four times from cyclohexane. The absence of any impurity emission in glass matrices at 77 K and verification that the fluorescence and excitation spectra in 77 K matrices agreed well, respectively, with the reported emission and the corresponding absorption spectra suggest that the purified samples were sufficiently pure for the experiment. Solvents used in the present experiment are all of spectroscopic grade.

Absorption spectra were measured with a Hitachi 2000-20 spectrophotometer and emission and excitation spectra were measured with a Hitachi 360-50S spectrophotometer or a Spex Fluorolog-2 (Model 211-SS) equipped with a photon-counting system. For most of the emission measurements, square 10-mm path length quartz cells were used. A triangle quartz cell was also used for the sample in some of the solvents, such as diiodomethane and $CS_2$, that show optical absorption in longer wavelengths. Raman peaks from the solvents were subtracted from the observed fluorescence spectra. Optical densities of the samples for emission measurements were always kept below 0.1. Temperature of the sample cells was controlled by a thermostated cell holder. Digital data were analyzed with Macintosh Quadra 650 loaded with a super PC memory and Power Macintosh G3 computers.

## Results and Discussion

It is now well established that the $1^1B_u$ excitation energy of polyenes decreases significantly with increasing solvent polarizability, while the $2^1A_g$ excitation energy is more nearly constant.[2,5] Reasonably accurate estimates of the fluorescence and absorption origin band centers can be derived by the Gaussian fitting procedure (vide infra). Solvent polarizabilities, $\alpha$, are approximated by $(n^2 - 1)/(n^2 + 2)$, where $n$ is the refractive

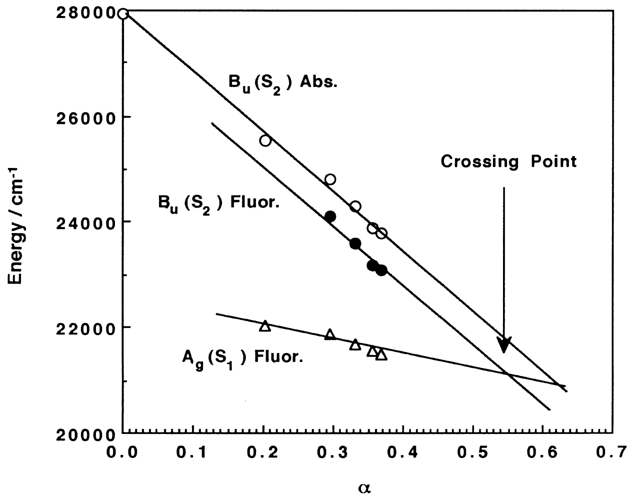

Fig. 1. The $S_2(1^1B_u)$ absorption (open circles), $S_2(1^1B_u)$ (closed circles) and $S_1(2^1A_g)$ fluorescence (open triangles) origin band centers determined by fitting Gaussians to the fluorescence and absorption spectra for 1,8-diphenyl-1,3,5,7-octatetraene in different solvents at room temperature, plotted as a function of the solvent polarizability $\alpha$.

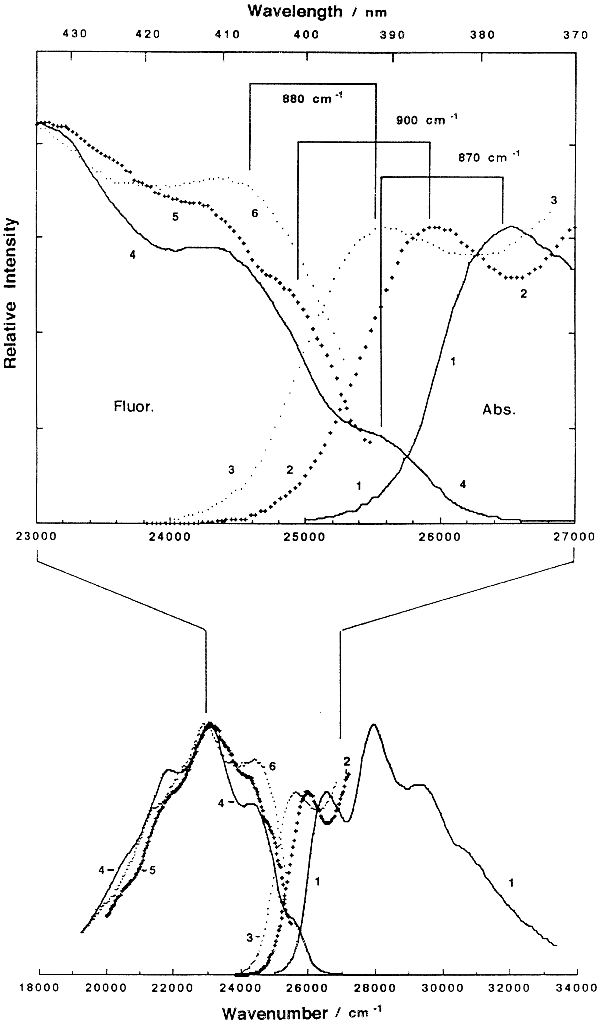

Fig. 2. Absorption (1, 2 and 3) and fluorescence spectra (4, 5 and 6) of 1,6-diphenyl-1,3,5-hexatriene in benzene (1 and 4), in a 1 : 1 mixture of benzene and $CS_2$ (2 and 5), and in $CS_2$ (3 and 6) at room temperature. Upper panel shows the spectra in expanded scale. The first absorption and the highest fluorescence bands are normalized, respectively, to common magnitudes. The apparent $S_2(1^1B_u)$ fluorescence and absorption origins are separated by 870–900 $cm^{-1}$. Higher-wavenumber parts of the spectra 5 and 6 are not shown, because of the strong scattering of the excitation light. Higher-wavenumber parts of the spectra 2 and 3 are not shown, because of the strong absorption of the solvents.

index of the solvent. Figure 1 shows the origin band centers determined by fitting Gaussians to the fluorescence and absorption spectra for DPO in different solvents at room temperature, plotted as a function of $\alpha$. Both of the $S_2(1^1B_u)$ fluorescence and absorption origins of DPO show significant and similar shifts to lower energy with increasing $\alpha$, while the location of the $S_1(2^1A_g)$ fluorescence origin is nearly invariant. Closer inspection of Fig. 1 reveals that the $2^1A_g$ energies show also a slight decrease with increasing $\alpha$. The slopes for the apparent $2^1A_g$ fluorescence origins plotted as a function of $\alpha$ is 3280 $cm^{-1}/\alpha$. Extrapolation of the $S_2(1^1B_u)$ and $S_1(2^1A_g)$ fluorescence origins provides the solvent polarizability value that can mark the inversion of the $2^1A_g$ and $1^1B_u$ levels, i.e., the inversion point. The variation of the $2^1A_g$ and $1^1B_u$ excitation energies of DPH against the solvent polarizabilities has been shown in a foregoing paper.[11] In the following we mention the changes of the fluorescence spectral patterns observed for DPH and DPO, when the $1^1B_u$ level approaches the $2^1A_g$ level.

**1,6-Diphenyl-1,3,5-hexatriene (DPH).** Figure 2 shows the absorption and fluorescence spectra of DPH in benzene, a 1 : 1 mixture of benzene and $CS_2$, and $CS_2$ at room temperature. It was shown in a foregoing paper that the band appearing at the blue shoulder of the strong $S_1(1^1A_g)$ fluorescence is the contribution from the $S_2(1^1B_u)$ fluorescence.[8] Extrapolation of the data shown in Ref. 11 predicts that the $2^1A_g$ level will be located at approximately 500 $cm^{-1}$ below the $1^1B_u$ level in $CS_2$ at room temperature.[11] Although in $CS_2$ the $2^1A_g$ level is located at energies below the $1^1B_u$ level, the measured spectrum looks just like the fluorescence from $S_2(1^1B_u)$, as is indicated by a good mirror-image relationship and a sufficient overlapping between the observed fluorescence and the $S_0(1^1A_g) \rightarrow S_2(1^1B_u)$ absorption bands. The Stokes shifts, i.e., the energy separations between the first absorption and emission bands, are always near 900 $cm^{-1}$ irrespective of the solvents used. That is, in $CS_2$ the emission of DPH in room temperature solution consists mostly of the $S_2(1^1B_u)$ fluorescence which occurs as the result of the thermal activation of the $2^1A_g$ state.[8]

Closer inspection of the emission spectra shown in Fig. 2 as well as those measured in different solvents reveals that the spectral pattern of the $S_1(2^1A_g)$ fluorescence changes slightly with increasing the solvent polarizability, along with the increase of the $S_2(1^1B_u)$ fluorescence intensity. Thus, we have analyzed the $S_1(2^1A_g)$ fluorescence spectral change quantitatively. In order to determine the band positions and relative intensities for the fluorescence and absorption, all the spectral data were fitted by sums of Gaussians, where the intensity $I(\nu)$

at wavenumber $\nu$ was assumed to have the form, $I(\nu) = I_0(\nu_0) \exp[-(\nu - \nu_0)^2/\sigma^2]$, where $n_0$ is the wavenumber at the Gaussian center, $I_0(\nu_0)$ is the amplitude and $\sigma$ is the width. When four Gaussians were fit by varying $I_0(\nu_0)$, $\nu_0$ and $\sigma$ to the first 4000 cm$^{-1}$ of the fluorescence spectra, the measured and calculated spectra were indistinguishable. In the case of intensity estimates for the $S_1(2^1A_g)$ fluorescence, the $S_2(1^1B_u)$ absorption spectrum, reflected so that the origin matched the origin of the $S_2(1^1B_u)$ fluorescence, was subtracted from the measured emission spectrum. Then, the resulting difference spectrum was fit by three Gaussians corresponding to the 0–0 and 0–1 for C–C and C=C stretch modes to get the Gaussian amplitudes corresponding to the $S_1(2^1A_g)$ fluorescence alone. This kind of analysis was performed for the spectra measured using a variety of solvents such as benzene, dioxane, and methanol.

The ratio of the first to the second Gaussian amplitude, $I_1/I_2$, used for fitting the $S_1(2^1A_g)$ fluorescence alone, after subtracting the contribution from the $S_2(1^1B_u)$ fluorescence, is plotted in Fig. 3 as a function of the energy separation between the $S_2(1^1B_u)$ and $S_1(2^1A_g)$ fluorescence origins, $\Delta E_{\mathrm{ff}}$. The ratio $I_1/I_2$ roughly corresponds to the ratio of the first to the second peak intensity of the $S_1(2^1A_g)$ fluorescence alone. One can see in Fig. 3 that $I_1/I_2$ increases with decreasing the $\Delta E_{\mathrm{ff}}$ value for DPH. When this ratio is extrapolated to $\Delta E_{\mathrm{ff}} = 0$ cm$^{-1}$, we obtain 0.84 ± 0.2 as the value for $I_1/I_2$. This value is very close to the ratio of the first to the second Gaussian amplitude fitted for the $S_0 \rightarrow S_2(1^1B_u)$ absorption spectrum of DPH in benzene (0.81) or in hexane (0.82). In other words, the shape of the $S_1(2^1A_g)$ fluorescence spectrum tends to resemble that of the $S_2(1^1B_u)$ fluorescence or the reflected $S_0 \rightarrow S_2(1^1B_u)$ absorption spectrum with decreasing $\Delta E_{\mathrm{ff}}$. This change can be attributed to the result of the strong vibronic coupling, by which an allowed character is introduced more effectively to the forbidden $2^1A_g$ state with decreasing the energy separation between the two states.[13]

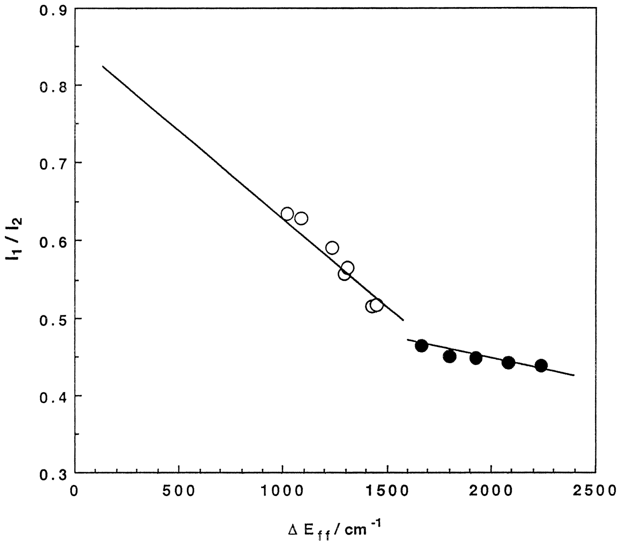

Fig. 3. Ratio of the Gaussian amplitudes, $I_1/I_2$, of the $S_1(2^1A_g)$ fluorescence plotted against the energy separation between the $S_2(1^1B_u)$ and $S_1(2^1A_g)$ fluorescence origins, $\Delta E_{\mathrm{ff}}$, for 1,6-diphenyl-1,3,5-hexatriene (open circles) and 1,8-diphenyl-1,3,5,7-octatetraene (closed circles).

**1,8-Diphenyl-1,3,5,7-octatetraene (DPO).** Extrapolation of the data shown in Fig. 1 predicts that the order of the $2^1A_g$ and $1^1B_u$ levels will be inverted at the solvent polarizability near 0.54. Figure 4 shows the absorption and fluorescence spectra of DPO in 1-bromonaphthalene ($\alpha$ = 0.368) and diiodomethane ($\alpha$ = 0.404) at room temperature. It is seen that the intensity of the $S_2(1^1B_u)$ fluorescence relative to that of the $S_1(2^1A_g)$ fluorescence increases with increasing the solvent polarizability. In diiodomethane the value for $\Delta E_{\mathrm{ff}}$ of DPO is es-

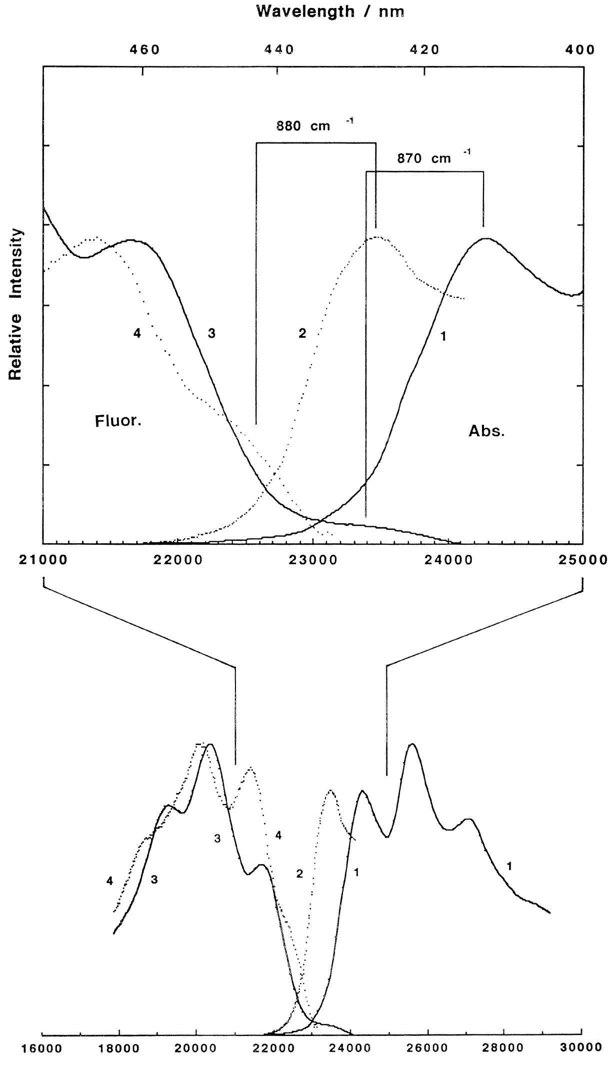

Fig. 4. Absorption (1 and 2) and fluorescence spectra (3 and 4) of 1,8-diphenyl-1,3,5,7-octatetraene in 1-bromonaphthalene (1 and 3) and in diiodomethane (2 and 4) at 20 °C. Upper panel shows the spectra in expanded scale. In upper panel the first bands of the spectra are normalized to a common magnitude, while in lower panel the highest bands are normalized to a common magnitude. The apparent $S_2(1^1B_u)$ fluorescence and absorption origins are separated by 870–880 cm$^{-1}$. Higher-wavenumber part of the spectrum 2 are not shown, because of the strong absorption of the solvents.

timated to be about 1200 $\mathrm{cm}^{-1}$. The fluorescence spectrum in diiodomethane shows that approximately 1/2 of the observed emission intensity involves the contribution from the $1^1B_u$ fluorescence. Although the full absorption spectrum of DPO could not be measured in diiodomethane due to the strong absorption of the solvent, we have already analyzed the $2^1A_g$ fluorescence spectra in benzene and 1-bromonaphthalene as well as in their mixtures.[9] The ratio of the first to the second Gaussian amplitude, $I_1/I_2$, used for fitting the $2^1A_g$ fluorescence alone is plotted also in Fig. 3 as a function of $\Delta E_{\mathrm{ff}}$. The ratio, $I_1/I_2$, increases slightly with decreasing $\Delta E_{\mathrm{ff}}$ for DPO. This observation can also be attributed to the effect of the strong coupling between the $2^1A_g$ and $1^1B_u$ states.[13] At present, solvents with the refractive index values over 1.7425 ($\alpha = 0.404$) are not available, but lowering the temperature and/or applying the high pressure may achieve the inversion of the two levels for DPO.[14]

## Conclusions

Fluorescence spectral change, observed when the $1^1B_u$ level approaches the $2^1A_g$ level, has been investigated for 1,6-diphenyl-1,3,5-hexatriene (DPH) and 1,8-diphenyl-1,3,5,7-octatetraene (DPO) in room temperature solution. In the neighborhood of the $2^1A_g$ and $1^1B_u$ level crossing point, the spectral shape of the $S_1(2^1A_g)$ fluorescence of DPH and DPO tends to resemble that of the $S_2(1^1B_u)$ fluorescence with decreasing the $2^1A_g$–$1^1B_u$ energy separation, along with a gradual increase of the $S_2(1^1B_u)$ fluorescence intensity. These effects are considered to be caused by the strong coupling between the $2^1A_g$ and $1^1B_u$ states. Solvent polarizability that achieves the inversion of the $2^1A_g$ and $1^1B_u$ levels is estimated to be 0.54 for DPO at 20 °C. It is shown for DPH that exclusive appearance of the $1^1B_u$ fluorescence does not necessarily indicate that the $1^1B_u$ level is located at energies below the $2^1A_g$ level at temperatures near room temperature.

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