

Excited State Localization or Delocalization in C₃-symmetric Amino-substituted Triphenylbenzene Derivatives

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Abstract: The site-to-site intramolecular excitation transfer and excitation trapping on one site in amino-substituted triphenylbenzene derivatives, which are characterized by a 3-fold symmetry, have been studied by fluorescence spectroscopy and time-resolved microwave conductivity (TRMC). The importance of dipole relaxation due to intramolecular energy transfer has been demonstrated in the interpretation of the limiting anisotropy on one hand and the change of the dipole moment and polarizability upon excitation on the other hand. The interpretation of the experimental results is based on the comparison of the molecules with C₃-symmetry with biphenyl model compounds.

Introduction

The properties of molecules or molecular complexes with a high degree of symmetry are of interest in a large number of research areas. Exciton migration via intramolecular excitation transfer¹ and trapping of the excited state upon incorporation of the chromophore in proteins and rigid matrixes² has been investigated in relation to the symmetry of these compounds, both theoretically,^{3,4} and experimentally using picosecond time-resolved polarized fluorescence,^{5,6} and transient absorption techniques.⁷ Moreover, the octupolar contribution to the large hyperpolarizability, found for several symmetric compounds,^{8,9} has led to a surge of interest in the nature of the excited state of these symmetric compounds.^{10,11}

In particular symmetry breaking upon excitation in molecules with 2-fold or 3-fold symmetry, leading to a polar singlet excited state, has been studied. Biaryl compounds such as bianthryl, for instance, are characterized by a polar excited state although they do not carry a specific donor or acceptor subunit.^{12–16} Also the excited states of symmetrical amino-substituted triphenyl-

benzene derivatives (see Figure 1) and triphenylphosphines,¹⁷ are characterized by an increased charge separation with respect to the ground state. Although the large fluorescence rate constant observed for most amino-substituted triphenylbenzene derivatives suggests the formation of a conjugated intramolecular charge transfer state,¹⁸ the similarity of the photophysical properties and the solvent dependence of the triphenylbenzene compound, pEFTP, and its biphenyl model compound, pEFBP (Figure 1), suggests the formation of a polar excited state which is localized in one branch of the triphenylbenzene derivative.¹⁹ The importance of geometrical changes to the excited-state deactivation of C₃-symmetric dyes has been demonstrated for triphenylmethane dyes.^{20–22} For these compounds an increased planarity in the singlet excited state compared to the propeller-like structure in the ground state has been suggested to explain their photophysical properties.²³

In addition to this localization of the excited state, the interaction of the three different branches is expected to result in an intramolecular excitation transfer among the three spatially

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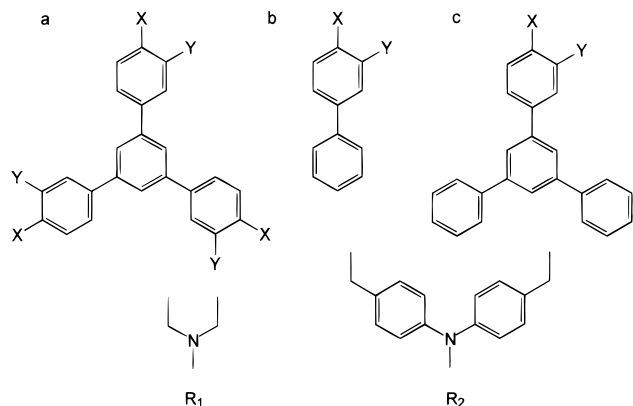


Figure 1. Structures of (a) the triphenylbenzene compounds pETP ($X = R_1$, $Y = H$), mETP ($X = H$, $Y = R_1$), pEFTP ($X = R_2$, $Y = H$), and mEFTP ($X = H$, $Y = R_2$); (b) the biphenyl model compounds mEBP ($X = H$, $Y = R_1$), pEFBP ($X = R_2$, $Y = H$), and mEFBP ($X = H$, $Y = R_2$); and (c) 1-pETP ($X = R_1$, $Y = H$).

different branches. Using fluorescence depolarization it is possible to observe this intramolecular excitation transfer because the latter process will be accompanied by a reorientation of the transition dipole resulting in partial depolarization of the emission. The rate of this reorientation of the transition dipoles has been observed for ruthenium(II) tris(bipyridine) complexes and proteins with a 3-fold symmetry by picosecond polarized transient absorption techniques.²⁴ If the transition dipoles are in the same plane as the central benzene ring and perpendicular to the symmetry axis, the law of additivity of polarization,^{25,26} yields a limiting anisotropy, r_0 , of 0.1 in the absence of rotational diffusion around any axis in the molecular plane. This has been observed in triphenylene and mesitylene, where a completely delocalized excited state with D_{3h} symmetry is formed.²⁷ If the intramolecular excitation transfer is slow with respect to the depopulation of the excited state, the limiting anisotropy will rise above 0.1.²⁸

For pEFTP cyclic voltammetry and coulometry show a unique, reversible, oxidation wave corresponding to a three-electron process. During the partial oxidation of pEFTP, the absorption of near-IR radiation results in the site-to-site migration of the hole by intramolecular electron transfer.²⁹ It has been demonstrated that this intervalence transition depends only to a limited extent upon substitution in the meta position of the central phenyl group.³⁰

The use of time-resolved microwave conductivity (TRMC) to estimate the change of the dipole moment and the change of the polarizability upon excitation has been demonstrated for several donor–acceptor and other compounds.^{31–34} In the

analysis of the TRMC transients knowledge of the dipole relaxation time is required in order to obtain absolute values for the dipole moment. It has been shown that for symmetric compounds such as pETP and mETP, the dipole relaxation time involves, in addition to the rotational diffusion time, a relaxation time due to intramolecular excitation transfer.³⁵

In this contribution the similarity between the photophysical properties of the tri-amino-substituted triphenylbenzene derivatives and their monosubstituted biphenyl or triphenylbenzene model compounds, Figure 1, is used to study the intramolecular excitation transfer in these symmetric compounds. The latter process is described by means of stationary fluorescence depolarization in propanediol glass and picosecond time-resolved fluorescence depolarization in benzene.

TRMC transients suggest large excited-state dipole moment and polarizability changes upon excitation of the C_3 symmetric compounds which are explained by the introduction of a picosecond intramolecular dipole relaxation path. The excited state properties of triphenylbenzenes and model compounds in combination with the TRMC transients are used consequently to estimate quantitatively the intramolecular excitation migration.

Experimental Section

See Supporting Information.

Results and Discussion

Photophysical Properties of mETP and mEBP. The absorption spectrum of mETP in acetonitrile at room temperature is characterized by maxima at 332 nm ($10\,600\text{ M}^{-1}\text{ cm}^{-1}$) and 256 nm ($111\,000\text{ M}^{-1}\text{ cm}^{-1}$). The solvent dependence of the emission maximum of mETP indicates that even in non-polar solvents the emission occurs from a state with a considerable dipole moment. The dipole moment has been estimated from the solvatochromic shift from diethyl ether to acetonitrile at $16.4 \pm 1.5\text{ D}$.¹⁸ Using TRMC measurements, we obtained a value of 14.1 D in benzene.³⁵ The large Stokes shift which is still observed in apolar solvents is attributed to the difference in equilibrium geometry between the excited state and the ground state. This effect was reported in detail for pEFTP and pEFBP.²³

More recently, a biphenyl model compound, mEBP, was synthesized. The photophysical properties of mEBP and its solvent dependence are similar to the properties of mETP (see Figure 2). The absorption spectrum at room temperature is not dependent on the solvent polarity and is characterized in acetonitrile by a strong absorption with a maximum at 247 nm ($210\,00\text{ M}^{-1}\text{ cm}^{-1}$) and a weak absorption at 330 nm ($2400\text{ M}^{-1}\text{ cm}^{-1}$) which matches the absorption spectrum of mETP in the same solvent. This similarity between mETP and mEBP suggests that upon excitation, the 3-fold symmetry disappears and the Franck–Condon excited state will probably be localized in one branch of mETP. Moreover, the molar extinction coefficients of mEBP are approximately one-third of the value obtained for mETP. Despite the structural differences between mETP and mEBP, the emission occurs in a similar wavelength region and shows a similar solvent dependence. Upon excitation, charge transfer leads to a polar excited state which induces a solvatochromic shift of the emission. The

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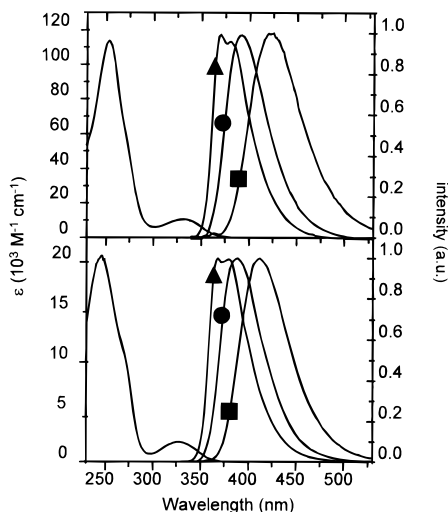


Figure 2. Absorption spectrum in acetonitrile and emission spectrum ($\lambda_{\text{ex}} = 320 \text{ nm}$) in isooctane (triangle), diethyl ether (circle), and acetonitrile (square) of mETP (top) and mEBP (bottom).

substitution of two ethylanilino groups in the meta position of the central phenyl ring in mETP has only a marginal effect upon the emission.

Fluorescence Depolarization of mETP and Its Biphenyl Model Compound mEBP in Propanediol Glass. The polarization of the emission of the biphenyl model compound mEBP has been measured in 1,2-propanediol at $-60 \text{ }^\circ\text{C}$. At this temperature at which the solvent forms a rigid glass, no depolarization of the emission occurs through rotational diffusion, and the anisotropy r , reaches the limiting anisotropy r_0 . When excitation occurs in the S_0 – S_1 absorption band ($\lambda_{\text{ex}} = 340 \text{ nm}$), the anisotropy increases from 0.22 to 0.33 at $11 \text{ }^\circ\text{C}$ and $-36 \text{ }^\circ\text{C}$, respectively, and reaches 0.35 at $-60 \text{ }^\circ\text{C}$. The limiting anisotropy is almost 0.4, which means that the transition dipoles of absorption and emission are close to collinear. Moreover, the anisotropy of mEBP stays constant over the whole emission wavelength region which indicates that only one emission (S_1 – S_0) contributes to the emission band. The minor difference between the anisotropy at $-36 \text{ }^\circ\text{C}$ and $-60 \text{ }^\circ\text{C}$ suggests that at temperatures below $-36 \text{ }^\circ\text{C}$ the molecular rotational diffusion is slow with respect to the fluorescence lifetime.

The anisotropy of mETP ($\lambda_{\text{ex}} = 350 \text{ nm}$), however, increases from 0.14 to 0.22 and to 0.28 when the temperature decreases from $0 \text{ }^\circ\text{C}$ to $-27 \text{ }^\circ\text{C}$ to $-60 \text{ }^\circ\text{C}$, respectively, and stays constant over the whole emission wavelength region. Moreover, the anisotropy reaches no plateau value around $-30 \text{ }^\circ\text{C}$ for mETP and is smaller than the model compound although the volume of mETP is larger than for mEBP and the lifetime of fluorescence is similar for both compounds (9.3 ns and 7.3 ns for mETP and mEBP in acetonitrile, respectively).

This indicates that in mETP depolarization occurs by another mechanism in addition to molecular rotation. This mechanism could be intramolecular excitation transfer which will rotate the transition dipole over 120° in a molecular plane. The limiting anisotropy r_0 , however, should be equal to 0.1 for molecules with a 3-fold symmetry when intramolecular excitation transfer redistributes the excitation energy among the three spatially degenerate transition dipole moments.²⁷ This means that, in the present case, the intramolecular excitation transfer is slow with respect to the lifetime of the excited state. The latter process becomes relatively more important at lower temperatures where the rotation of the molecule is blocked.

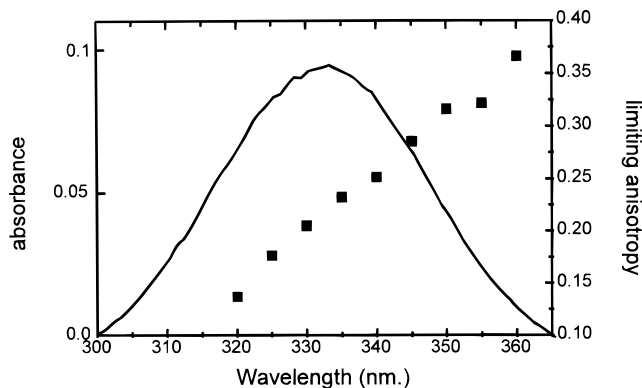


Figure 3. Increase of the limiting anisotropy of mETP in 1,2-propanediol at $-60 \text{ }^\circ\text{C}$ upon excitation at the red edge of the S_0 – S_1 absorption band ($\lambda_{\text{em}} = 430 \text{ nm}$).

In contrast to what was observed for mEBP, the limiting anisotropy increases when the excitation occurs at the red edge of the S_0 – S_1 absorption spectrum of mETP (Figure 3). In this excitation region, the emission becomes more polarized and a limiting anisotropy close to the maximum value of 0.4 can be found.

This cannot be due to overlap with other transitions or to scattered light because the emission was monitored at 390 nm where no scattered light is observed. Also, when the excitation spectra were obtained at a longer emission wavelength the limiting anisotropy r_0 observed became larger. This increase of r_0 indicates that excitation transfer between the three branches becomes less efficient when excitation occurs at the red edge of the absorption spectrum. A possible explanation of this increase could be a reduction of the 3-fold symmetry of mETP in 1,2-propanediol at low temperatures. Under these conditions the solvent configuration around, as well as the phenyl–phenyl and amino–phenyl torsion angles in the three branches, could be slightly different. If this configuration persists for a time which is long compared to the excited-state lifetime, the excited state of the three branches will be stabilized to a different extent by dipole–dipole interactions or hydrogen bonding on one hand, and because of geometrical interactions on the other hand (Figure 4A). Here we assume that solvation of the three branches of mETP is to a certain extent uncorrelated. At $-60 \text{ }^\circ\text{C}$, the excitation migration will be determined by high-frequency vibrations of the solute and solvent matrix surrounding the polar excited state.

Under these conditions excitation at the red edge of the absorption band will excite that branch of mETP where the dipolar excited state has the largest stabilization. Hence excitation transfer to other branches will become endergonic. This will slow the rate of excitation transfer and will increase the anisotropy. On the other hand, excitation at shorter wavelengths will excite other branches where the dipolar excited state experiences a smaller solvent stabilization and hence excitation transfer to other branches will become exergonic. This will increase the rate of excitation transfer and decrease the anisotropy (Figure 4B).

Time-Resolved Fluorescence Depolarization of pEFTP and Its Biphenyl Model Compound pEFBP in Benzene. The time-resolved depolarization of the fluorescence of pEFTP and pEFBP at room temperature in benzene was obtained and analyzed as described in the experimental section. The decays were obtained with a time increment of 3.7 ps per channel so that excited-state processes slower than 20 ps could be resolved. The fluorescence depolarization decay of the biphenyl

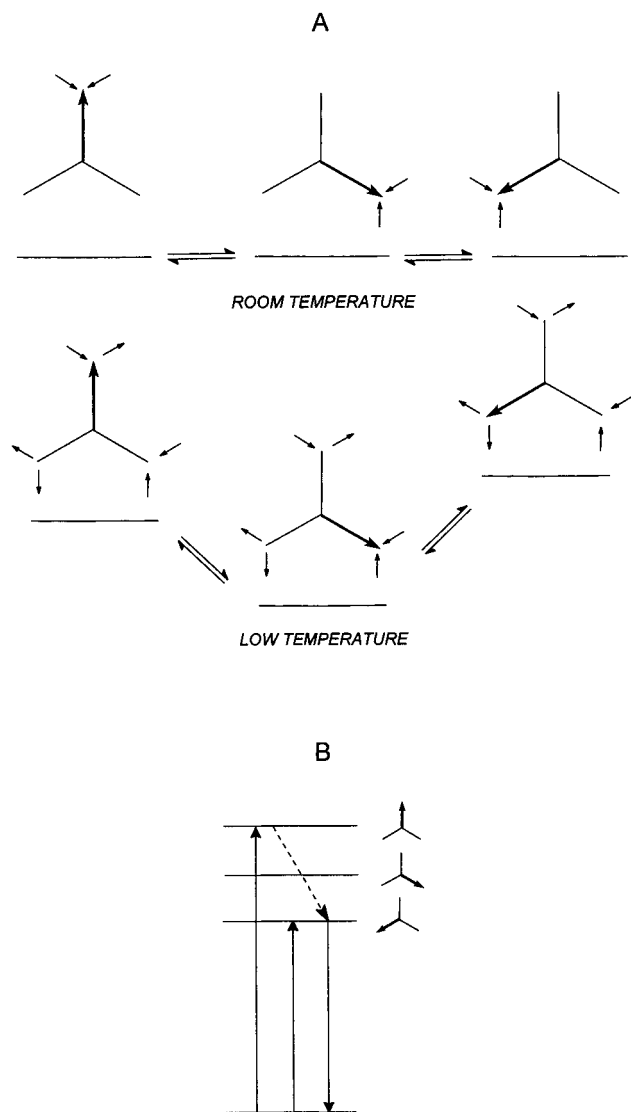


Figure 4. (A) Scheme of the transition dipole relaxation process of mETP at room temperature and at low temperature. The large and small arrows represent the orientation of the transition dipole and the solvent, respectively. (B) Relaxation of the transition dipole moment at low temperature upon excitation at short or long wavelengths.

pEFBP could be analyzed as a monoexponential fluorescence decay ($\tau = 1.068 \pm 0.003$ ns) and a single rotational relaxation time ($\Theta = 90 \pm 8$ ps) with good acceptable statistical parameters. The β value of 0.31 ± 0.02 corresponds to the limiting anisotropy. The latter property indicates a nearly parallel orientation of the absorption and emission transition dipole for the biphenyl compound pEFBP in benzene at room temperature, similar to that suggested for mEBP in propanediol glass at -60 °C.

The fluorescence depolarization decay of the C_3 -symmetric pEFTP could be analyzed as a monoexponential fluorescence decay ($\tau = 1.059 \pm 0.003$ ns) with one rotational relaxation time $\Theta = 320 \pm 40$ ps. The small β -value of 0.077 ± 0.004 , however, suggests an additional relaxation mechanism in the excited state through intramolecular excitation transfer. No improvement of the fit, however, is observed when a second relaxation time is introduced. Despite the picosecond resolution of the experimental setup, no direct measurement of the relaxation time associated with the latter process could be obtained. The relaxation time Θ can be assigned to the

rotational diffusion out of plane of pEFTP in benzene at room temperature.

Time-Resolved Microwave Conductivity. On photoexcitation, a transient change of the permittivity was observed for all compounds in benzene solution (Figure 5). The transients measured at the resonance frequency, f_0 , are proportional to the change in the dielectric loss, $\Delta\epsilon''$, and are characterized by a rise, followed by a slow decay. Initially after excitation, mainly the singlet excited state contributes to the observed transient, whereas at longer times after the excitation, the signal is due to the triplet excited state. Lifetimes for the singlet and triplet state were obtained separately from the fluorescence decay, using the single-photon counting technique, and from the TRMC transients at long times after the laser pulse. The fast component of the TRMC signal corresponds to the singlet lifetime. This justifies the attribution of the dielectric loss to the dipolar character of both S_1 and T_1 and their amplitude can be used to calculate the charge separation in the excited state. The transient changes of the dielectric loss recorded for pEFTP, mEFTP, and mETP were compared to their biphenyl model compounds, pEFBP, mEFBP, and mEBP. The transients of pETP were compared to those of 1-pETP, the singlet properties of which are closer to those of pETP than to those of a biphenyl model derivative of pETP.

From the fits, μ_S^2/Θ can be determined, where μ_S is the dipole moment of S_1 and Θ is the dipole relaxation time (Table 1). Normally the dipole relaxation time is determined by the rotational diffusion, and can be calculated using an empirical expression based on an assumed shape. Because of their comparable shape, Θ will not depend significantly on the substitution (meta or para) for isomeric compounds. The ratio of the dipole moments of the meta and para compounds will therefore be given to a good approximation, if $(\omega\Theta)^2$ (where ω is the reciprocal radian frequency of the microwaves ($1/\omega \approx 15$ ps) used) was larger than 1, by:

$$\frac{\mu_S^{\text{para}}}{\mu_S^{\text{meta}}} \approx \sqrt{\frac{\left(\frac{\mu_S^2}{\Theta}\right)_{\text{para}}}{\left(\frac{\mu_S^2}{\Theta}\right)_{\text{meta}}}} \quad (1)$$

This ratio can also be derived from solvatochromism because the solvent cavity radius depends also only slightly on the position of the substitution. Although agreement between the TRMC and solvatochromism result is found for pEFBP versus mEFBP, this is not the case for pEFTP versus mEFTP. Although an almost equal dipole moment is suggested by solvatochromism, the ratio $\mu_S^{\text{pEFTP}}/\mu_S^{\text{mEFTP}}$ in the TRMC experiment (Table 1) is 2.02. On substituting for Θ the a priori calculated value of the rotational relaxation time of a sphere-shaped molecule,³⁶ the dipole moment for the biphenyl model compounds calculated is close to that obtained from solvatochromism.¹⁸ The use of a sphere to model the rotational relaxation is supported by the correspondence with the experimentally obtained relaxation times in benzene by time-resolved fluorescence depolarization. The dipole moments of the triphenylbenzene derivatives determined in the same way are, however, larger than those obtained from the solvatochromic data. This discrepancy can be resolved if the dipole relaxation time of the triphenylbenzene derivatives is in fact much shorter than the rotational relaxation time of these molecules. This will be the case if intramolecular excitation transfer between the three

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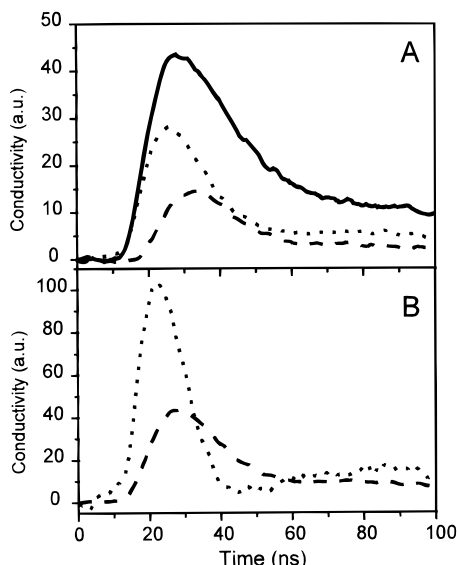


Figure 5. (A) Typical TRMC transients observed on flash photolysis of a solution of 1-pETP in benzene at the cavity resonance frequency f_0 (full line), and at the upper, f_+ (dashed), and lower, f_- (dotted), half-power frequency. (B) The sum $\Sigma\pm$ (dashed), and difference, $\Delta\pm$ (dotted), combinations of the transients monitored at the half-power frequencies for the traces in (A). $\Sigma\pm$ is proportional to $\Delta\epsilon''$ and $\Delta\pm$ is a function of $\Delta\epsilon'$.

Table 1. Decay Time, Dipole Moment, Rotational Relaxation Time, and Polarizability Volume

compound	τ_{FL} (ns)	μ_e^2/Θ (D ² /ps)	μ_e^2/a^3 (D ² /Å ³) ^a	Θ_R (ps) ^b	μ_S (D) ^c	$\Delta\alpha'$ (Å ³) ^d
pEFTP	1.3	1.58	1.00	244	19.7	583
pEFBP	1.2	0.54	0.96	94	7.2	186
mEFTP	4.2	0.39	1.01	244	9.7	103
mEFBP	4.1	0.33	0.95	94	5.7	87
pETP	9.7	0.42	0.54	130	7.5	370
1-pETP	10.7	0.75	0.84	94	8.5	130
mETP	6.2	0.79	1.03	130	10.2	176
mEBP	2.9	1.06	0.81	56	8.0	92

^a Slope of the emission maximum versus the solvent polarity; a is the solvent cavity radius. ^b The calculated rotational relaxation time for a dipole oriented in the plane of a sphere-shaped molecule. ^c Singlet dipole moment based on $\Theta = \Theta_R$. ^d Overall polarizability volume.

branches occurs. Hence the rotational (Θ_R) and intramolecular (Θ_I) dipole relaxation times will both contribute to the overall dipole relaxation time Θ :

$$\frac{1}{\Theta} = \frac{1}{\Theta_R} + \frac{1}{\Theta_I} \quad (2)$$

From the sum, $\Sigma\pm$, of a pair of TRMC transients observed at the half-power frequencies f_+ and f_- , $\Delta\epsilon''$ can also be obtained and yields results identical to the measurements on f_0 . From the difference, $\Delta\pm$, of these transients the change of the real component of the permittivity, $\Delta\epsilon'$, can be obtained. This change is related to the change of the polarizability, $\Delta\alpha$, upon excitation (for more details see reference 34) via:

$$\Delta\epsilon' = \frac{N_*[\epsilon(\infty) + 2]^2 \Delta\alpha}{9\epsilon_0} \quad (3)$$

In eq 3, N_* is the concentration of excited molecules, $\epsilon(\infty)$ is the relative dielectric constant of the solvent which can be equated with the square of the refractive index, and ϵ_0 corresponds to the permittivity of vacuum. It is most convenient

to discuss them in terms of the change of the polarizability volume, $\Delta\alpha'$, given by:

$$\Delta\alpha' = \frac{\Delta\alpha}{4\pi\epsilon_0} \quad (4)$$

The value of $\Delta\alpha'$ is a measure of the degree of delocalization of the electron wave function in the excited state. The polarizability volume changes of the triphenylbenzene and the model compounds are listed in Table 1. The para-substituted compounds display a much larger $\Delta\alpha'$ compared to the corresponding meta compounds which suggests that the electronic delocalization is affected by the position of the substitution. More surprising is the much larger polarizability of the symmetric triphenylbenzene derivatives, compared to the model compounds, despite their similar photophysical properties. For instance, $\Delta\alpha'$ amounts to 186 Å³ for pEFBP but is no less than 583 Å³ for pEFTP. To explain this large discrepancy, we assume that for the model compounds the dipole relaxation process can only occur by relaxation of the whole molecule via tumbling, characterized by $\Theta = \Theta_R$. This value was used to calculate μ_S from the TRMC experiments and yielded values in agreement with those from the solvatochromism. However, as already discussed, this was not the case for the triphenylbenzene derivatives, the Θ of which must be much shorter than the Θ_R , indicating the occurrence of flip-flop intramolecular relaxation process.

Because of the fast dipole relaxation in flip-flop, $\Delta\epsilon'$ has to be considered to consist not only of an electronic contribution, $\Delta\epsilon'_e$, but also a dipole contribution, $\Delta\epsilon'_D$. Thus:

$$\Delta\epsilon' = \Delta\epsilon'_e + \Delta\epsilon'_D \quad (5)$$

in which:

$$\Delta\epsilon'_e = \frac{N_*[\epsilon(\infty) + 2]^2 \Delta\alpha_e}{9\epsilon_0} \quad (6)$$

$$\Delta\epsilon'_D = \frac{N_*[\epsilon(\infty) + 2]^2}{27\epsilon_0 k_B T} \left[\frac{\mu_*^2}{1 + (\omega\Theta_*)^2} - \frac{\mu_0^2}{1 + (\omega\Theta_0)^2} \right] \quad (7)$$

In eq 7, the subscripts 0 and * refer to the ground state and the excited state, respectively. If $\mu_0 = 0$, which is a realistic assumption for the triphenylbenzene compounds, eq 7 can be simplified, because the last term drops out. By using eqs 3 and 4, $\Delta\epsilon'_i$ can be expressed as $\Delta\alpha'_i$, in which the subscript i can be either e or D.

Normally, if $\Theta = \Theta_R$, the denominator in eq 7 is large and $\Delta\epsilon'_D$ will be close to zero and can therefore be neglected. In the case of the biphenyl model compounds where Θ is indeed large (Table 1), $\Delta\alpha'_e$ will be overestimated by no more than 5 Å³, due to neglect of the dipolar contribution. This is within the experimental error. The large polarizability of the triphenylbenzene derivatives suggests that in addition to the electronic component (eq 6), the dipolar term (eq 7) contributes to the observed polarizability. To quantify this contribution, the similarity of the photophysical properties between the symmetric triphenylbenzene compounds (TP) and the related biphenyl compounds (BP) is used and it is assumed reasonable that both will have an equal electronic polarizability:

$$\Delta\alpha'_e^{TP} = \Delta\alpha'_e^{BP} \quad (8)$$

Table 2. Calculated Dipole Moment μ_S and Intramolecular Dipole Relaxation Time Θ_I (Flip-Flop) for the Triphenylbenzene Derivatives Assuming $\Delta\alpha'_D{}^{TP} = \Delta\alpha'^{TP} - \Delta\alpha'^{BP}$

compound	$\Delta\alpha'_e{}^{BP}$ (\AA^3)	$\Delta\alpha'_D{}^{TP}$ (\AA^3)	μ_S (D)	Θ (ps)	Θ_I (ps)
pEFTP	186	397	7.9	9.3	9.7
mEFTP	87	16	4.9	56.3	73.1
pETP	130	240	5.5	4.2	4.3
mETP	92	84	5.3	22.4	27.1

With this assumption and using eqs 3 and 4 to evaluate from $\Delta\alpha'_D$ to $\Delta\epsilon'_D$, $\Delta\epsilon'_D{}^{TP}$ can be estimated for the triphenylbenzene derivatives. These results indicate an important difference between the para- and meta-substituted compounds. Whereas the polarizability has mainly an electronic origin for the meta compounds, the dipolar contribution is the main contribution for the para compounds. From the calculated $\Delta\epsilon'_D{}^{TP}$, Θ can be estimated via:

$$\frac{\Delta\epsilon''}{\Delta\epsilon'_D} = \omega\Theta \quad (9)$$

The dipole relaxation is an order of magnitude faster than the rotational dipolar relaxation, Θ_R . Thus Θ must be almost completely determined by the intramolecular excitation transfer. The flip-flop mechanism occurs in the subnanosecond time region with an intramolecular dipole relaxation time, Θ_I , of 10 ps for pEFTP and 73 ps for mEFTP. Using the same procedure to estimate Θ_I for pETP and mETP yields relaxation times of 4 and 27 ps, respectively. The difference between pEFTP and mEFTP or pETP and mETP is attributed to the smaller interaction between the three amino sites in the meta-substituted compounds, compared to the para-substituted compounds.

The dipole moment of the excited state can be obtained from the analysis of the TRMC transients at the resonance frequency, f_0 , and the dipole relaxation time, which includes the molecular rotational diffusion and the flip-flop relaxation process and is given in Table 2. These dipole moments are more plausible than those reported in Table 1 where only Θ_R was considered.

The fast dipole relaxation has been suggested not only for mETP in propanediol at -60°C but also for other triphenylbenzene derivatives in benzene at room temperature. For pEFTP, it has been demonstrated by time-resolved fluorescence depolarization that excitation transfer between the three branches occurs at times shorter than 20 ps.

Conclusion

The localized character of the polar excited state of amino-substituted triphenylbenzene derivatives with a 3-fold symmetry has been studied. The similar absorption and emission properties of the symmetric compounds and the model compounds indicate that the excited state reached immediately after excitation and vibrational relaxation is localized in one branch of the 3-fold symmetric compound. During the lifetime of the excited state, however, intramolecular excitation transfer occurs between three energetically degenerate excited states. This redistribution

of transition dipoles will depolarize the emission to a certain extent. Hence the limiting anisotropy of mETP is smaller than 0.4 which has been observed for the model compound mEBP and indicates collinear transition dipoles for the latter compound. Because of this flip-flop mechanism, the relaxation of the dipole involves, in addition to the rotational diffusion, an intramolecular relaxation path. The importance of this process has been demonstrated in the analysis of the TRMC transients where it is necessary to obtain a similar excited-state dipole moment for the triphenylbenzene and its model compound consistent with the solvatochromic shift of the emission.

If the exciton was redistributed completely among the three sites during the lifetime of the excited state, the limiting anisotropy, however, would be 0.1. The larger value experimentally obtained for mETP suggests that the flip-flop between different sites in 1,2-propanediol at -60°C is slow with respect to the other deactivation processes of S_1 . This probably is due to a relatively small interaction between the three branches. Moreover, in a rigid glass matrix, the three sites will be stabilized to a different extent in the polar excited state so that the degeneracy disappears. This is translated in an increase of the limiting anisotropy when excitation occurs in the red edge of the absorption band. The exciton will be trapped in the most stable site from where emission mainly will occur. For pEFTP in benzene at room temperature the limiting anisotropy is close to 0.1 and suggests a fast intramolecular excitation transfer compared to the excited-state lifetime.

Upon excitation, a relatively large increase of the polarizability which consists of an electronic and dipolar contribution, is observed for all compounds. Although for the model compounds the dipolar contribution is negligible, the large dipolar contribution for the symmetric compounds indicates an intramolecular excitation transfer in the time range of the reciprocal radian frequency ω . The dipole relaxation time associated with the latter process has been estimated to be approximately 10, 73, 4, and 27 ps for pEFTP, mEFTP, pETP, and mETP, respectively. The meta- or para-substitution pattern, as well as the molecular geometry of the molecule and the solvent reorganization around the branches, influences the interaction between the three amino sites and hence determines the rate of intramolecular excitation transfer.

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Supporting Information Available: Experimental details (3 pages). See any current masthead page for ordering and Internet access instructions.