Photoinduced charge separation and broken symmetry in Franck-Condon excited $\pi\pi'^*$ states of tetraphenylpentatetraenes

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Abstract

Franck-Condon excited state dipoles and polarizabilities of tetraphenylpentatetraene (TPPT) and tetrakis-(2-methoxyphenyl)-pentatetraene (OMTPPT) have been investigated by means of electrooptical absorption measurements (EOAM) in cyclohexane solution at 298K. The optical absorption spectra of TPPT and OMTPPT show two well separated bands at $\lambda \sim 340$ nm (strong) and $\lambda \sim 420$ nm (weak) which can be ascribed to the $\pi\pi^* 1^1 B_2 \leftarrow 1^1 A_1$ transition (allowed) and the $\pi\pi'^* 1^1 A_2 \leftarrow 1^1 A_1$ transition (forbidden). The EOA experiment reveals excited state dipoles of 5 and 7×10^{-30} Cm for TPPT and OMTPPT in their $\pi\pi'^*$ excited states. These dipoles are parallel to the long molecular axis and to the transition dipole.

INTRODUCTION

The investigation of the optical absorption of molecules in solution in an externally applied electric field (electrooptical absorption measurements, EOAM) yields information on electric dipoles and polarizabilities in vibronic ground and excited states, transition dipole directions, transition polarizabilities and transition hyperpolarizabilities (ref. 1). In a series of EOA experiments we investigated the localized excitation of a bichromophore and the excited state dipoles and polarizabilities of all-trans polyenes and other centrosymmetric molecules (refs. 2–4). Recently, EOA experiments were performed on phototautomerizing systems (refs. 5 and 6). In this study we investigate the excited state dipoles and polarizabilities of two $[4N]\pi$ cumulenes, tetraphenylpentatetraene, TPPT, and tetrakis-(2-methoxyphenyl)-pentatetraene, OMTPPT (Fig. 1).
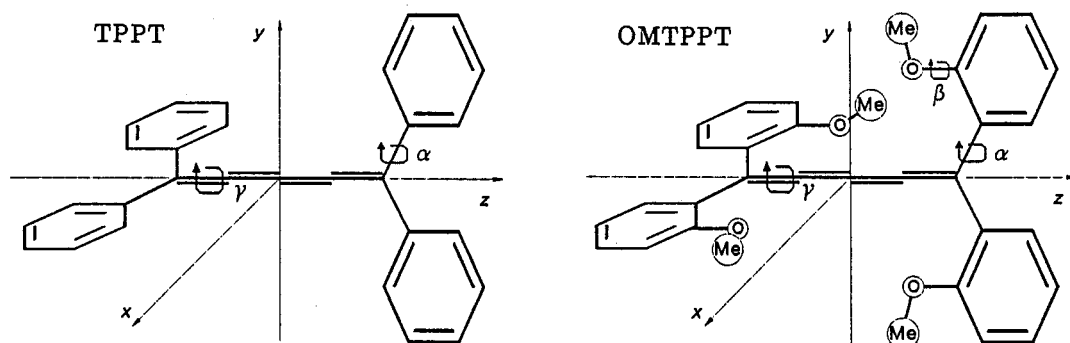

Fig. 1. Abbreviations, structure formulae, and definition of the molecule-fixed coordinate system of the investigated molecules. TPPT and OMTPPT have conformational degrees of freedom (see text).

Symmetric tetraphenyl derivatives of pentatetraene are known since the work of Kuhn et al. (ref. 7) and were selected for the present study for reasons of stability and spectral position of absorption bands. The electronic structure of these $[4N]\pi$ cumulenes is characterized by two equivalent and mutually perpendicular π systems, π and π'. The lowest excited configuration $(e)^3(e)^1$ gives rise to two 'charge resonance' states of type $\pi\pi'^*$, $1^1 B_1$ and $1^1 A_2$, and two 'locally excited' states of type $\pi\pi^*$, $1^1 B_2$ and $2^1 A_1$. Similar states are also present in the perpendicular conformation of 9,9'-bianthryl (BA). However the state ordering in tetraphenylpentatetraenes and BA is different. The lowest excited singlet state of BA in apolar solvents is an excitonic state of type $\pi\pi^*$, $1^1 B_2$. Effective torsional potentials of this state in liquid solution were determined in two recent studies by a simultaneous FC and band shape analysis of temperature dependent fluorescence spectra (refs. 8 and 9).

The S_1 states of tetraphenylpentatetraenes on the other hand are of $\pi\pi'^*$ type. The two $\pi\pi'^*$ states are near degenerate (refs. 10 and 11) and therefore susceptible to any internal or external perturbation due to different conformations of the terminal phenyl groups or different solvent environments at the two π subsystems. Such perturbations could lead to a directed electron transfer between the two inequivalent π subsystems upon excitation. The aim of this study is to determine the extend of charge transfer in the low lying $\pi\pi'^*$ transitions of TPPT and OMTPPT from the FC excited state dipole by means of the EOA experiment.

THEORY

For a comprehensive review on the determination of molecular electric properties from dielectric, refractometric, and electro-optical absorption measurements we refer the reader to articles of Liptay (refs. 1, 12 – 14). The basic equations were summarized recently (ref. 6). The relations that are most important in the context of this work are given below. The effect of an external electric field E_a on the optical absorption spectrum of a dilute solution can be described by the following equations (ref. 1)

$$L = L(\chi,\tilde{\nu}) = (1/E_a^2)\,[\kappa^E(\chi,\tilde{\nu}) - \kappa(\tilde{\nu})]/\kappa(\tilde{\nu}) \tag{3}$$

where κ and κ^E denote the molar absorption coefficient in absence and presence of the applied field, χ is the angle between the direction of E_a and the electric field vector of the incident light, and $\tilde{\nu}$ is the wavenumber. For an isolated electronic band L is given by (refs. 1 and 2)

$$L = Dr + \tfrac{1}{6}Es + Frt + Gst + Hru + Isu \tag{4}$$

where $r = (2 - \cos^2\chi)/5$, $s = (3\cos^2\chi - 1)/5$, $t = (1/hc)\,(\kappa/\tilde{\nu})^{-1}\,d(\kappa/\tilde{\nu})/d\tilde{\nu}$, and $u = (1/2h^2c^2)\,(\kappa/\tilde{\nu})^{-1}$ $d^2(\kappa/\tilde{\nu})/d\tilde{\nu}^2$. The functions t and u can be calculated from the first and second derivative of the absorption spectrum $(\kappa/\tilde{\nu})$. h is Planck's constant, and c the speed of light in vacuum. The electro-optical coefficients D, E, F, G, H and I may be interpreted microscopically as follows (refs. 1 and 2)

$$D = (1/kT)\,R^{(1)}\mu + S^{(1)} \tag{5}$$
$$E = (1/k^2T^2)[3(m\mu)^2 - \mu^2] + (1/kT)[3(m\alpha m) - \mathrm{Tr}(\alpha)] + (3/kT)R^{(2)}\mu + 3S^{(2)} \tag{6}$$
$$F = (1/kT)\mu\Delta\mu + \tfrac{1}{2}\mathrm{Tr}(\Delta\alpha) + R^{(1)}\Delta\mu \tag{7}$$
$$G = (1/kT)(m\mu)(m\Delta\mu) + \tfrac{1}{2}m\Delta\alpha m + \tfrac{1}{2}R^{(2)}\Delta\mu \tag{8}$$
$$H = (\Delta\mu)^2 \tag{9}$$
$$I = (m\Delta\mu)^2 \tag{10}$$

m is the unit vector in the direction of the transition dipole in the molecule-fixed frame. μ and α are the dipole moment and the static polarizability of the electronic ground state, and $\Delta\mu$ and $\Delta\alpha$ the change of the dipole moment and the static polarizability upon excitation to the Franck-Condon (FC) excited state. The scalars $S^{(1)}$ and $S^{(2)}$ and the vectors $R^{(1)}$ and $R^{(2)}$ describe effects of the applied electric field on the magnitude of the transition dipole in terms of transition polarizability and hyperpolarizability. The quantities μ, α, $\Delta\mu$ and $\Delta\alpha$ in eqs. 5 - 10 refer to the molecule in solution. Local field corrections within the extended Onsager model (refs. 13 and 14) yield the dipoles μ_g and μ_a and static polarizabilities α_g and α_a of the free molecule in its electronic ground state (index g) and FC excited state (index a).

RESULTS

<u>Tetraphenylpentatetraene (TPPT)</u>. The optical absorption spectrum $\kappa/\tilde{\nu}$ of TPPT was measured in cyclohexane solution at $T = 298$ K (Fig. 2, full line). Two bands are observed at $\tilde{\nu} = 29850$ cm^{-1} and
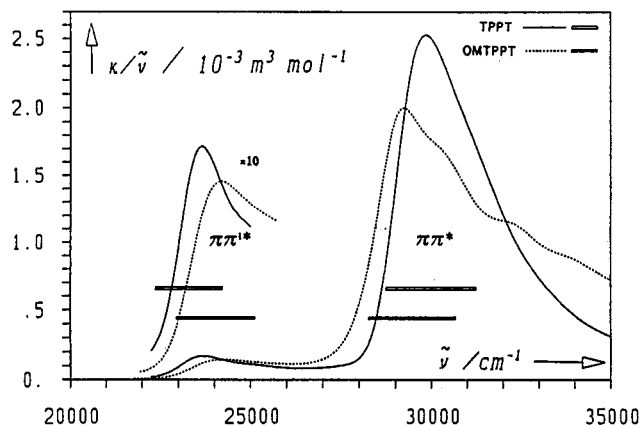

Fig. 2. Optical absorption spectra of TPPT (full line) and OMTPPT (dotted line) in cyclohexane at $T = 298$K. The bars indicate the intervals of the EOA measurement. The $\pi\pi'^*$ transition is also shown on an expanded scale.

23700 cm^{-1} which are assigned to the allowed $1^1B_2 \leftarrow 1^1A_1$ transition of type $\pi\pi^*$ and to the forbidden intramolecular CT band $1^1A_2 \leftarrow 1^1A_1$ of type $\pi\pi'^*$, respectively. Electrooptical absorption spectra of TPPT in cyclohexane solution (Fig. 3) were recorded for both bands in the wavenumber intervals indicated by the horizontal bars in Fig. 2. From the EOAM spectra we determined the electrooptical coefficients D to I by general linear least squares optimization. Results are listed in Table 1.

TABLE 1. Results of electrooptical absorption measurements on TPPT and OMTPPT.

band		TPPT $\pi\pi'^*$	TPPT $\pi\pi^*$	OMTPPT $\pi\pi'^*$	OMTPPT $\pi\pi^*$
D	/10^{-20} V^{-2}m^2	-19 ± 2	0 ± 1	-10 ± 2	-4 ± 2
E	/10^{-20} V^{-2}m^2	166 ± 14	282 ± 5	191 ± 11	234 ± 9
$(E-6D)$	/10^{-20} V^{-2}m^2	280 ± 14	282 ± 5	251 ± 1	258 ± 9
F	/10^{-40} CV^{-1}m^2	159 ± 4	99 ± 2	109 ± 4	94 ± 5
G	/10^{-40} CV^{-1}m^2	130 ± 4	48 ± 2	107 ± 4	65 ± 5
H	/10^{-60} C^{2}m^2	62 ± 8	21 ± 8	147 ± 14	107 ± 13
I	/10^{-60} C^{2}m^2	60 ± 8	8 ± 8	115 ± 14	39 ± 13
$\alpha_g^\perp$	/10^{-40} CV^{-1}m^2	(50)	(50)	77 ± 10	77 ± 11
$\alpha_g^{\parallel}$	/10^{-40} CV^{-1}m^2	95 ± 6	97 ± 6	122 ± 10	122 ± 11
$\Delta\alpha^\perp$	/10^{-40} CV^{-1}m^2	17 ± 3	29 ± 3	-7 ± 12	8 ± 16
$\Delta\alpha^{\parallel}$	/10^{-40} CV^{-1}m^2	138 ± 10	56 ± 4	55 ± 96	47 ± 59
$\Delta\mu^\perp$	/10^{-30} Cm	0.0 ± 2.1	2.7 ± 1.2	4.3 ± 1.4	6.2 ± 0.9
$\Delta\mu^{\parallel}$	/10^{-30} Cm	5.3 ± 0.4	2.1 ± 0.9	7.6 ± 0.8	4.5 ± 0.8

The given error limits include an estimate of the possible error due to the unknown conformational distribution. The polarizability given in parenthesis is estimated (see text).
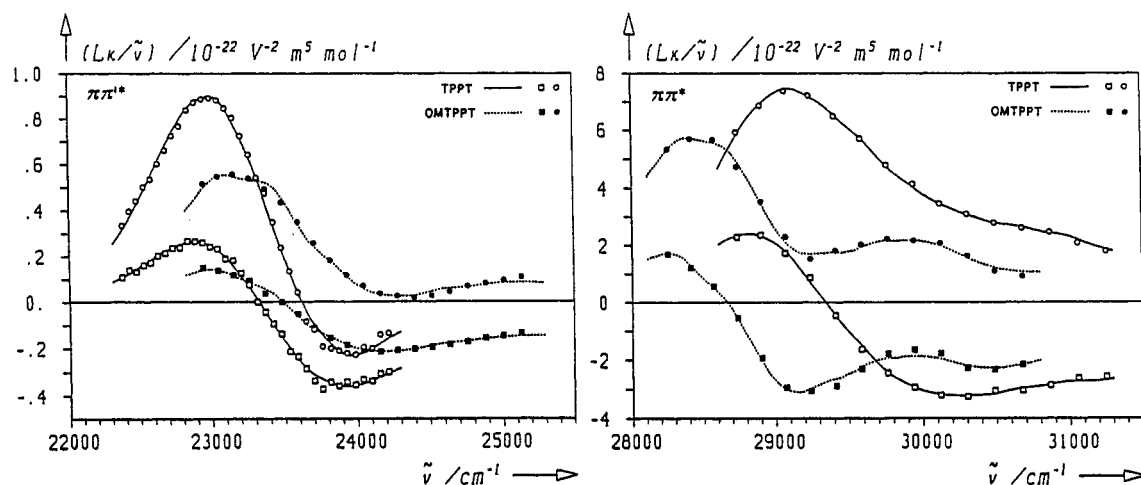

Fig. 3. Electrooptical absorption spectra of TPPT (full line) and OMTPPT (dotted line) in cyclohexane at $T = 298$K. The figure shows experimental data points for two polarizations (o,o: $\chi = 0°$; □,□: $\chi = 90°$) and calculated curves obtained by a general linear least squares fit.

In the evaluation of molecular properties from the EOA coefficients we label quantities being parallel and perpendicular to the long molecular axis (z) by $\parallel$ and $\perp$, respectively. The semi-axes $a_x = a_y = a^\perp$, and $a_z = a^{\parallel}$ of ellipsoidal Onsager cavities were estimated from average bond lengths, van der Waals radii (ref. 15) as well as crystallographic data (ref. 16) for TPPT. The principal components $A_{gx} = A_{gy} = A_g^\perp$, and $A_{gz} = A_g^{\parallel}$ of the optical polarizability tensor of TPPT were estimated from group and bond polarizabilities (ref. 15) and the known polarizability of bis-adamantylidene-propadiene, BAPD (ref. 3). The EOAM experiments detects static polarizabilities α_g which we approximate by $\alpha_g = A_g$ for TPPT.

Due to its approximate D_{2d} symmetry and the absence of polar substituents we take the ground state dipole μ_g of TPPT to be zero. Torsions of the phenyl groups by angles α distroy the idealized D_{2d} symmetry. However the molecule remains apolar since all partial dipoles mutually cancel each other. In the approximation $\mu_g = 0$ eqs. 5 and 6 simplify to

$$D = S^{(1)} \tag{15}$$

$$E = (1/kT)[3(\tilde{m}\alpha m) - \text{Tr}(\alpha)] + 3S^{(2)} \tag{16}$$

If the transition polarizability and the transition hyperpolarizability term $S^{(2)}$ could be neglected (as often) then the coefficient E would contain only the anisotropy of the ground state polarizability tensor. Since this quantity is independent of the studied electronic transition the coefficients E of the $\pi\pi'^*$ and the $\pi\pi^*$ band should be equal. Table 1 shows that this is not the case, i.e. $S^{(2)}$ must not be neglected. It can be shown that $S^{(2)}$ may be approximated for long chain molecules according to

$$S^{(2)} = 2\,S^{(1)} \tag{17}$$

Using eq. 17 we have from eqs. 15 and 16 $(E - 6D) = (1/kT)[3(\tilde{m}\alpha m) - \text{Tr}(\alpha)]$. The excellent agreement of this quantity for both bands justifies the approximation eq. 17. From $(E - 6D) > 0$ and $\alpha_g^{\|}$ > $\alpha_g^{\perp}$ it can be concluded that the transition dipole is essentially parallel to the long molecular axis, i.e. $m = e_z$, for both transitions, $\pi\pi'^*$ and $\pi\pi^*$. The nonvanishing coefficient D of the $\pi\pi'^*$ band is remarkable. It indicates a nonzero transition hyperpolarizability, since $D = S^{(1)} \approx (1/\mu_{ga})^2 \mu_{ga} \cdot \beta_{ga}$, where β_{ga} is the vector part of the transition hyperpolarizability.

With the estimated values of the polarizability components $\alpha_g^{\perp}$ it is possible to calculate the long-axis polarizability $\alpha_g^{\|}$ from $E - 6D$. The excited state polarizabilities α_a and dipoles μ_a can now be obtained from eqs. 7 - 10 where all terms containing the ground state dipole μ or the transition polarizability, i.e. $R^{(1)}$ and $R^{(2)}$, may be neglected. Results for the changes of the polarizability and the dipole upon electronic excitation, $\Delta a^{\perp} = \alpha_a^{\perp} - \alpha_g^{\perp}$, $\Delta a^{\|} = \alpha_a^{\|} - \alpha_g^{\|}$, $\Delta\mu^{\perp} = \mu_a^{\perp} - \mu_g^{\perp}$, $\Delta\mu^{\|} = \mu_a^{\|} - \mu_g^{\|}$, are given in Table 1. A strong increase of the polarizability parallel to the transition dipole is observed. $\alpha_a^{\|}$ is 2.4 and 1.6 times as large in the $\pi\pi'^*$ and $\pi\pi^*$ excited states as compared to the ground state.

Most important, we find a considerable excited state dipole $\mu_a^{\|}$ in the $\pi\pi'^*$ excited state while $\mu_a^{\perp}$ is zero within experimental error. $\mu_a^{\|}$ and $\mu_a^{\perp}$ of the $\pi\pi^*$ state are small. This result clearly indicates symmetry breaking, i.e. mixing of the close lying 1^1B_1 and 1^1A_2 states due to internal and/or external distortions of the TPPT molecules.

Tetramethoxyphenylpentatetraene (OMTPPT). The optical absorption spectrum of OMTPPT (Fig. 1, dotted line) is quite similar to the TPPT spectrum. The weak $\pi\pi'^*$ band is observed at 24270 cm^{-1} and shifted hypsochromic by ~580 cm^{-1} with respect to the TPPT transition. The strong $\pi\pi^*$ band is located at 29240 cm^{-1} and shifted bathochromic by ~610 cm^{-1}. Electrooptical absorption measurements on OMTPPT were recorded and analyzed similarly to TPPT. Results are given in Fig. 3 as well as Table 1. Similar to the case of TPPT we find that $E - 6D$ is identical for the two transitions. OMTPPT also shows a significant change of the dipole $\Delta\mu^{\|}$ parallel to the transition dipole. However this is less clearly interpreted because of considerable perpendicular contributions $\Delta\mu^{\perp}$.

DISCUSSION

Structural considerations. According to van't Hoff's rule one expects pentatetraenes to be linear and the terminal bonds of the cumulene chain to lie in mutually perpendicular planes. This structure has been observed in X-ray diffraction studies on TPPT and bis-(2,2,6,6-tetramethyl-cyclohexylidene)-propadiene (ref. 16). The angles between any three adjacent carbon atoms of the pentatetraene chain were found to deviate from 180° by less than 2°. For unsubstituted pentatetraene (C_5H_4) a bent structure with a distortion of about 8° of the central CCC angle was proposed from quantum chemical calculations including electron correlations (ref. 17). However the question whether pentatetraene is bent has not been finally answered (ref. 18). For the purposes of this study it is adequate to assume a linear structure of the pentatetraene chain in TPPT and OMTPPT.

A more serious problem is posed by the conformational degrees of freedom that are present in TPPT and OMTPPT (Fig. 1). Due to steric interactions between the geminal phenyl groups distortions from coplanarity occur. The phenyl groups in TPPT and OMTPPT may be twisted by angles α, in

OMTPPT the methoxy groups may also be twisted by angles β and, finally, the terminal bond planes may be twisted by an angle γ. We have performed AM1 calculations (ref. 19) in order to characterize the conformational behaviour of the tetraphenylpentatetraenes. Torsions of about $\gamma \sim 15°$ may be reached within thermal energy kT (~ 200 cm^{-1}). In the minimum obtained for TPPT all phenyl rings are twisted by about the same angle of $\alpha \sim 34°$. This may be compared to the crystal conformation where twist angles of $\alpha_1 = 16.4°$, $\alpha_2 = 51.3°$, $\alpha_3 = 28.2°$ and $\alpha_4 = 42.5°$ have been observed (ref. 16). Remarkably, in the AM1 minimum obtained for OMTPPT all phenyl rings are twisted to an almost perpendicular conformation, $\alpha_1 = 95°$, $\alpha_2 = -85°$, $\alpha_3 = -95°$, and $\alpha_4 = 84°$. This is probably due to the steric requirements of the methoxy groups. The methoxy groups themselves are twisted by only $\beta_1 = \beta_2 = -12°$, $\beta_3 = \beta_4 = 12°$ from the phenyl planes. The conformation $\beta = 0°$ is known to represent the minimum of the torsional potential in anisole. Ab initio calculations (ref. 20) show that the torsional potential rises rapidly between $\beta = 0°$ and $50°$. It then becomes flat and has a small minimum at $\beta = 90°$. The torsional barrier was calculated to be a few kcal/mole. Using the RHF/3–21G torsional potential calculated by Spellmeyer et al. (ref. 20) we obtain an average twist angle of the methoxy group in anisole of $<\beta> = 20°$ at $T = 298$ K. The calculations show that the torsional potentials connected with the angles α, β and γ are flat so that a broad distribution of conformations will be present in solution at room temperature. This was taken into account in the evaluation of the molecular properties in Table 1.

Symmetry considerations. In this section we consider the symmetry and electronic structure of pentatetraenes on the basis of an idealized D_{2d} symmetry of these $[4N]\pi$ cumulenes. In particular unsubstituted pentatetraene (C_5H_4) is treated as the suitable reference system. The z axis is defined parallel to the cumulene chain (cf. Fig. 1). Pentatetraene contains to equivalent, mutually perpendicular π systems, π and π'. The π molecular orbitals are doubly degenerate. Each degenerate pair forms a basis for the irreducible representation e. The lowest excited configuration is $(e)^3(e)^1$ and decomposes according to $E \times E = A_1 + A_2 + B_1 + B_2$. The resulting excited states may be approximated by the following configuration state functions

$$|2^1A_1> \sim {}^1\Phi(\pi \to \pi^*) + {}^1\Phi(\pi' \to \pi'^*) \qquad (18)$$
$$|1^1B_2> \sim {}^1\Phi(\pi \to \pi^*) - {}^1\Phi(\pi' \to \pi'^*) \qquad (19)$$
$$|1^1B_1> \sim {}^1\Phi(\pi \to \pi'^*) + {}^1\Phi(\pi' \to \pi^*) \qquad (20)$$
$$|1^1A_2> \sim {}^1\Phi(\pi \to \pi'^*) - {}^1\Phi(\pi' \to \pi^*) \qquad (21)$$

where the symbol ${}^s\Phi(a \to b)$ represents a spin adapted singly excited configuration of multiplicity s arising by promotion of one electron from orbital a to orbital b. Semiempirical quantum chemical calculations by Mehlhorn (ref. 10) suggest the state ordering $1^1A_2 \approx 1^1B_1 < 2^1A_1 < 1^1B_2$ for long chain $[4N]\pi$ cumulenes. 1^1B_2 is the only state that is electric dipole allowed. The transition dipole of the absorption $1^1B_2 \leftarrow 1^1A_1$ is aligned parallel to the cumulene chain.

The optical absorption spectra of TPPT and OMTPPT show two well seperated bands. We assign the strong band near $\lambda = 340$ nm to the allowed $1^1B_2 \leftarrow 1^1A_1$ transition of type $\pi\pi^*$ and the weak band at about $\lambda = 420$ nm to the forbidden transition $1^1A_2 \leftarrow 1^1A_1$ of type $\pi\pi'^*$, respectively. These assignments are based on the results of the EOAM experiment which shows that both transitions are polarized parallel to the cumulene chain. The intensity of the long-wave transitions may be caused by dynamical (Herzberg-Teller vibronic coupling) or static distortions of the cumulene systems. A symmetry analysis of the normal vibrations of pentatetraene shows that the reducible representation Γ_{vib} of the 21 normal coordinates decomposes according to $\Gamma_{vib} = 4A_1 + B_1 + 4B_2 + 6E$. The component μ_z of the dipole operator transforms like B_2 in D_{2d}. Thus the transition $1^1A_2 \leftarrow 1^1A_1$ would be allowed by HT coupling through a B_1 mode and the transition $1^1B_1 \leftarrow 1^1A_1$ by HT coupling through an A_2 mode. Since there is no A_2 vibrational mode in C_5H_4 we are led to the assignment $1^1A_2 \leftarrow 1^1A_1$ for the long-wave band in the case of dynamic distortions. The intensity inducing B_1 mode corresponds to the twisting vibration of the C_5H_4 molecule. A static distortion by an angle γ of C_5H_4 along the B_1 torsional mode reduces the molecular symmetry from D_{2d} to D_2. The state correlations for $D_{2d} \to D_2$ are $A_1 \to A$, $A_2 \to B_1$, $B_1 \to A$, $B_2 \to B_1$. μ_z transforms like B_1 in D_2. Therefore the transition $1^1A_2 \leftarrow 1^1A_1$ gains intensity upon static distortion, $1^1B_2 \leftarrow 1^1A_1$ stays allowed, while $1^1B_1 \leftarrow 1^1A_1$ stays forbidden. Summarizing, from the experimentally observed, long axis polarization we are led to the assignment $1^1A_2 \leftarrow 1^1A_1$ for the weak long-wave transition irrespective of the cumulene B_1 distortion being dynamic or static in nature. Clearly, the symmetry considerations made for C_5H_4 do not rigorously apply to the flexible molecules TPPT and OMTPPT. Nevertheless they provide a useful basis for the classification of the observed spectral transitions.

Now we investigate the influence of a B_2 perturbation on the excited states. Any perturbation that makes the two π systems in the pentatetraenes inequivalent has a component of this irreducible representation. The perturbation may be external, i.e. due to different local environments at the two π subsystems. Or the perturbation may be internal, i.e. caused by different conformations of the

phenyl groups at the ends of the cumulene chain. In any case, a B_2 perturbation that is static on the timescale of the absorption process will mix the close lying excited states $|1^1A_2\rangle$ and $|1^1B_1\rangle$ to a state $|\psi\rangle = c_A |1^1A_2\rangle + c_B |1^1B_1\rangle$. This state has a nonzero expectation value of the electric dipole $\langle\psi|\mu_z|\psi\rangle = 2\,c_A\,c_B\,\langle 1^1A_2|\mu_z|1^1B_1\rangle$, that may be interpreted by a partially directed, photoinduced electron transfer between the two mutually perpendicular π systems. It is expected that the close lying states 1^1A_2 and 1^1B_1 are especially sensitive against B_2 perturbations and that their mixing may produce considerable dipole moments because of the charge transfer character of these states (ref. 11). A crude estimation assuming charge separation on the distance of one cumulenic double bond ($\sim$0.13 nm) yields an excited state dipole of $\mu_a \sim 21\times10^{-30}$ Cm. This is 3 to 4 times larger than the observed values in Table 1.

CONCLUSION

A comparative electrooptical absorption study of $\pi\pi^*$ and $\pi\pi'^*$ transitions in tetraphenylpentatetraenes was presented. The EOA experiment detects FC excited states. Therefore the results are not influenced by solvent relaxations. Nonzero excited state dipoles were found for the $\pi\pi'^*$ excited states indicative of partial electron transfer between the perpendicular π systems upon electronic excitation.

Acknowledgement

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