

SPECTROSCOPIC PROPERTIES OF [n.1]-METACYCLOPHANENYLIDENES

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Abstract: The syntheses and fluorescence emission spectra of a series of bis-[n.1]-metacyclophanenylidenes (**1**: n=4; **2**: n=5; **3**: n=6) are discussed. The photophysical properties of **1-3** are compared to a model compound, tetrakis-(*m*-tolyl)-ethylene, **4**. Varying the degree of phenyl ring torsional freedom drastically alters the fate of the arylethylene excited singlet. Compound **1** exhibits strong fluorescence at room temperature ($\Phi_f = 0.43$), while **2** and **3**, though over ten times less fluorescent ($\Phi_f(\mathbf{2}) = 0.03$, $\Phi_f(\mathbf{3}) = 0.01$), are still at least ten times more fluorescent than **4** ($\Phi_f < 0.001$). These results are suggestive of the importance of phenyl ring torsional motion in the nonradiative decay of the excited singlet state. The light-induced ring closure, typical of arylethylenes, is attenuated in **1-3**.

INTRODUCTION

Excited state twisting is potentially a viable method for controlling the number of electrons transferred in a photochemical event, since clear electrochemical precedent exists for geometrically-linked multiple electron exchange. When electrooxidation (or reduction) is followed by a rapid chemical reaction (even one as simple as geometric twisting), a redox intermediate may be formed which is more easily oxidized (or reduced) than the starting material. A second electron will then flow easily (an ECE route) and a multielectron redox reaction is observed via electrochemical methods.

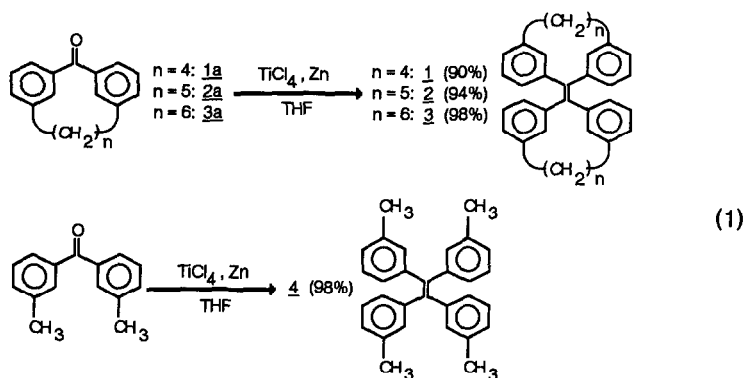
Inherently, excited states are both more easily oxidized and reduced than are ground states. Redox-induced geometric alteration can often be predicted, therefore, by observing the photophysical properties of the relevant system. Tetraphenylethylenes (TPEs) are excellent vehicles for testing this relationship for they are known to participate in multiple electrochemical redox reactions, when appropriately substituted.^{1,2} We have examined therefore a series of conformationally restricted tetraphenylethylenes to determine the effect of geometric restraint on their photophysical properties.

SYNTHESIS

Cyclophanes **1-3** and the model compound, tetrakis-(*m*-tolyl)-ethylene, **4** were obtained by the titanium-induced reductive coupling reaction³ of the corresponding [n.1]-metacyclophane-ones, **1a-3a**, and 3,3'-dimethylbenzophenone, respectively, according to eq. 1. The synthesis of **1a** and **2a** has been described previously⁴ and **3a** was obtained in a similar manner. A detailed description of the syntheses of **1-3** will be described elsewhere.⁵

PHOTOPHYSICAL AND PHOTOCHEMICAL PROPERTIES

The predominant deactivation processes of the excited singlet (S_1) of TPEs include fluorescence,⁶ *cis* - *trans* isomerization,¹ dihydrodiphenylphenanthrene formation,⁷ and intersystem crossing.^{6c} The fluorescence quantum yield of TPE in fluid media at room temperature is on the order of 10^{-3} .^{1,6} Barbara and coworkers^{9a} measured a fluorescence emission lifetime for TPE of 6 ps. Their time resolved variable temperature/viscosity emission measurements lead them to the conclusion that a number of conformational processes were taking place on the excited



state energy surface. These geometry changes involve phenyl ring torsional movement and olefinic twisting. The transient absorption experiments of Greene^{9b} are consistent with the time resolved emission results of Barbara et al. Greene observed two transient absorptions following a 0.5 ps (305 nm) photolysis pulse. The 640 nm absorption was determined to have a lifetime of 5 ± 1 ps and was attributed to an absorption of the vertical excited singlet. The second absorption appearing at 423 nm exhibited a 6 nm blue shift on the timescale of the decay of the 640 nm band and a lifetime of 3.0 ± 0.5 ns. The 423 nm band was assigned to a non-fluorescent twisted geometry on the excited state manifold. Recently, Schilling and Hilinski^{9c} demonstrated the zwitterionic nature of the twisted TPE excited singlet.

Olsen and Buckles⁷ have measured the quantum yield of dihydrodiphenylphenanthrene formation (Φ_{DPP}) for a series of substituted TPEs and noted a decrease in Φ_{DPP} with a decrease in the energy of S_1 . Φ_{DPP} ranged from 0.01-0.03 in their series. The combination of the degenerate *cis-trans* isomerization,¹ dihydrodiphenylphenanthrene formation,⁷ and intersystem crossing^{6c} for TPE accounts for approximately 98% of the deactivation of the excited singlet state.

The work presented here demonstrates the importance of phenyl ring torsional freedom in the deactivation of the excited singlet state of TPEs.

The S_1 energies of **1-4** were estimated by the overlap of the excitation and emission spectra, and ranged from 73-75 kcal/mol. If Φ_{DPP} for **4** \approx Φ_{DPP} for TPE ($\Phi_{\text{DPP}} = 0.02$), then Φ_{DPP} for **1-3** should have about the same value. However, qualitative experiments show that Φ_{DPP} for **1** is nearly zero. The excited singlet energy of **1** cannot be responsible for this behavior. The inefficiency of DPP formation from S_1 of **1** must be the result of a substantial barrier encountered during the carbon-carbon bond formation process. This barrier may be the result of bond angle strain imposed by the rigid nature of the phenyl ring orientations in **1**.⁸

The sensitivity of Φ_f to phenyl ring torsional motion may be examined by comparing Φ_f for the series **1-4** (Table 1). Adding one methylene unit to each bridge in **1** (**2**) results in a decrease in Φ_f by a factor of 14, and addition of two methylene units to **1** (**3**) decreases Φ_f by a factor of 40. Removal of the chain (**4**) decreases Φ_f by at least 430 fold. The low Φ_{DPP} , the large Φ_f (Table 1) and the decrease in internal conversion of **1** relative to TPE is the result of the rigidity of **1**. Clearly, the current mechanism of olefinic twisting in S_1 and internal conversion to S_0 for arylenes^{6,9a,10} must be revised to account for the importance of phenyl ring torsional motion. Our results suggest that substantial phenyl ring torsional movement is necessary to bring the molecule in the S_1 manifold to the critical geometry (twisted olefinic bond) required for radiationless conversion to the ground state. In the series **1-4**, increased phenyl ring torsional freedom results in faster conversion to the critical geometry and decreased fluorescence.

Table 1. Photophysical Properties of 1-4

Cmpd.	$\lambda_{\text{max}}^{\text{abs(a)}}$	$\lambda_{\text{max}}^{\text{em (a)}}$ (77K)	Stokes Shift (cm^{-1}) (77K)	$\phi_f^{(b)}$	P
<u>1</u>	344	434 (429)	6028 (5760)	0.43	0.036
<u>2</u>	342	469 (432)	7918 (6092)	0.03	0.090
<u>3</u>	340	471 (444)	8180 (6889)	0.01	0.130
<u>4</u>	315	491 (429)	11379 (8436)	<0.001	0.360

^a In nanometers, solutions in 2-methyl-tetrahydrofuran

^b Solutions in THF with matched absorbance at the exciting wavelength using 9,10-diphenylanthracene as the actinometer

The Stokes shifts for systems 1-4 are indicative of the trend in torsional freedom. The smallest Stokes shift recorded in this series is that for 1, almost one-half that of 4. The small Stokes shift for 1 (6082 cm^{-1}) indicates a relatively small difference in the S_1 and S_0 minima for 1. The emission maximum of 1 changes only 5 nm on going from a rigid glass at 77 K to fluid solution at 298 K (Table 1). Compound 2 shows a emission maximum difference of 37 nm, while that for 3 is 27 nm. By comparison, 4 changes 62 nm.

The emission polarization (P) is inversely related to the excited state lifetime^{6b} by the Perrin equation (eq. 2) ($k =$ Boltzmann constant, $T =$ temperature, $\tau =$ lifetime of excited molecule, $v =$ volume of solvated molecule, $\eta =$ viscosity).

$$1/P - 1/3 = (1/P_0 - 1/3)(1 + kT\tau / v\eta) \quad (2)$$

Examination of the emission polarization ratios of 1-4 (Table 1) shows an increase in P with an increase in bridge length: $P(\underline{1}) < P(\underline{2}) < P(\underline{3}) < P(\underline{4})$. Therefore, it is expected that the emissive lifetime should decrease in the same order. Preliminary time-resolved emission studies confirm that the emissive lifetimes fall in the order: $\underline{1} > \underline{2} > \underline{3} > \underline{4}$. Further studies of these molecules are underway.

Acknowledgement. We are grateful to the U. S. Dept. of Energy, Office of Basic Energy Sciences, for support of this work.

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(Received in USA 26 April 1988)