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Equilibration between the Fluorescent and Zwitterionic Phantom States in Alkyl-Substituted Tetraphenylethylenes[1]

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The cis–trans photoisomerization of alkenes is one of the most extensively investigated and best characterized photoreactions.[2] The partitioning and dynamics in the stilbene family of arylalkenes often serve as a model for this reaction type.[3] Recent photophysical studies[4] of the related arylalkene, tetraphenylethylene (TPE) and its analogs, have demonstrated (1) zwitterionic character in the twisted excited singlet state ($^1p^*$) and (2) that phenyl–vinyl torsional motion strongly influences the isomerization dynamics. In an attempt to further characterize the development of zwitterionic character on the excited-state potential energy surface, we undertook a systematic investigation of *p*-methyl substituent effects on the vertical and twisted excited-state dynamics. As expected, the results indicate zwitterionic character in $^1p^*$. More significantly, the results demonstrate that the fluorescent and twisted excited states are in equilibrium in nonpolar solvents and that their interconversion modulates the fluorescence spectrum and quantum yield.

The kinetics of $^1p^*$ decay in arylalkenes **1–4** (Scheme I) was measured using picosecond optical calorimetry (POC).[4e,5] This technique detects variations in the sample refractive index produced by heat released during the formation and decay of transient intermediates. The $^1p^*$ decay rate constants, k_R, of **1**, **3**, and **4**, in which both ethylenic carbons are identically substituted, are roughly constant (Table I). In contrast, the $^1p^*$ decay rate constant of **2**, with di-*p*-tolyl and diphenyl substitution of the ethylene carbons, is 2–3 times larger. Placement of both *p*-tolyl groups on the same carbon stabilizes the zwitterionic configuration in which the cation localizes on the more electron -rich half of the twisted state. On the basis of a previously established correlation[4e] between the $^1p^*$ decay rate constant and the $^1p^*$–^1p energy gap, the gap in **2** is estimated to be 1.0 ± 0.5 kcal/mol smaller than in **1**. As the ^1p energy decreases slightly with parasubstitution,[6] the $^1p^*$ energy in **2** is at least 1 kcal/mol lower than in **1**.

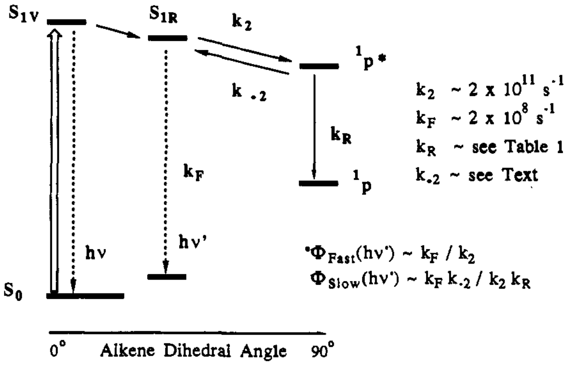
Surprisingly, the fluorescence quantum yield in **2** is reduced more than the $^1p^*$ lifetime (Table I), and the maximum in the emission blue shifts by ~40 nm (Figure 1). Picosecond fluorescence studies[4b] demonstrated that the luminescence from TPE is composed of a featureless emission from the vertical excited state, S_{1V}, which decays within 10 ps, and a bathochromically shifted, featureless emission from a conformationally relaxed excited state, S_{1R}. The "relaxed" emission is observed even under conditions where $^1p^*$ is not formed.[4b] It is the emission from S_{1R} that is strongly diminished in **2** relative to **1**, **3**, and **4**.

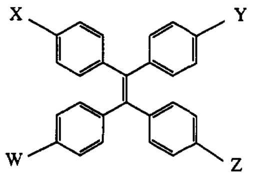
Table I. Arylalkene Data in Pentane at 294 K

alkene	$\Phi_{Fl}/\Phi_{Fl}(1)^a$	λ_{max}/nm^b	$k_R/10^8\ s^{-1\ c}$
1	1.00	542	6.0
2	0.14	500	18.5
3	1.04	542	8^d
4	1.29	542	8^d

[a] Quantum yield of the total fluorescence from each alkene relative to **1**. [b] Wavelength of maximum fluorescence intensity. [c] Determined using picosecond optical calorimetry. [d] Current precision of this value warrants one significant digit.

Scheme I





1: W=X=Y=Z=H
2: W=Z=H X=Y=CH_3
3: W=H Z=CH_3 X≠Y=(CH_3, H)
4: W=X=Y=Z=CH_3

A decrease in the $S_{1R} \rightarrow {}^1p^*$ activation free energy in **2** of 1 kcal/mol could explain the reduced quantum yield of emission from S_{1R}.[7] However, there is an alternate explanation that finds precedent in two studies of TPE derivatives which reported biexponential fluorescence decays from S_{1R}.[4b,d] The energies of S_{1V} and $^1p^*$ for **1** in pentane are ~77 and ~67 kcal/mol, respectively.[4d,e,8] These values bracket the energy of S_{1R} and suggest that an S_{1R}–$^1p^*$ equilibrium is possible. A simple model for the kinetics and fluorescence quantum yield in this system (Scheme I) predicts biexponential fluorescence decays from S_{1R}. The S_{1R}–$^1p^*$ equilibrium is established during the faster decay; the equilibrium mixture decays with the slower rate constant.

The fluorescence decay from **1** in methylcyclohexane (MCH) at 520 nm (S_{1V} and S_{1R})[4b] exhibits two components which contribute nearly equally to the steady-state fluorescence intensity at this wavelength. The slow component (S_{1R}) decays with a rate constant of $6 \times 10^8\ s^{-1}$. This is identical to the $^1p^*$ decay rate constant determined by picosecond optical calorimetry[4e] or by transient absorption spectroscopy[4c] and demonstrates that S_{1R} and $^1p^*$ are in equilibrium. The faster component in the fluorescence decay follows the instrument response of our digitizer (~0.9 ns).

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(7) Presumably, *p*-methyl substitution decreases the $^1p^*$ energy in **2** by stabilization of the zwitterion. If the $S_{1R} \rightarrow {}^1p^*$ activation barrier is decreased by this same amount in **2**, but not in **3**, then the barrier stabilization must also be polar in origin. It seems unlikely that the barrier between the nonpolar S_{1R}[4d] and zwitterionic $^1p^*$ states would have as complete charge separation and as extensive energy stabilization as the $^1p^*$ state.

(8) The energy of S_{1V} is estimated from the crossing point of the normalized arylalkene absorption and emission spectra in ether. In this solvent, emission from the vertical state predominates. For each arylalkene, the absorption spectra in pentane and ether are shifted by less than 1 nm.

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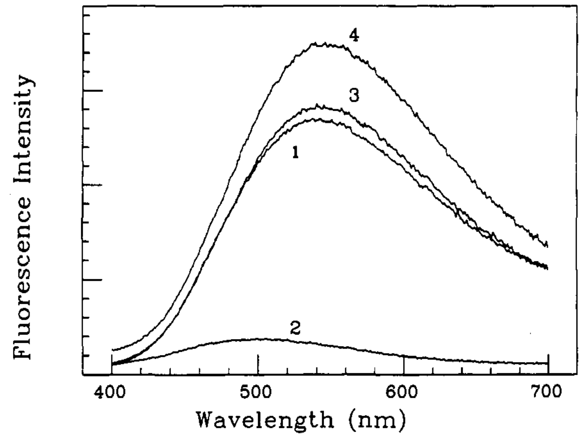

Figure 1. Steady-state fluorescence spectra of **1**–**4** in pentane excited at 310 nm. The spectrum of **4** contains a noticeable contribution from the 5,6-di-*p*-tolyl-2,9-dimethylphenathrene cyclization product in the wavelength range 340–440 nm.

It contains emission from S_{1V} and from S_{1R} prior to the attainment of equilibrium with $^1p^*$. The slow component makes up most of the fluorescence decay at 650 nm. The fluorescence decay from **4** is analogous to that from **1**, with a slow decay rate constant of 8×10^8 s^{-1}.

For **2** in MCH, the fluorescence decay follows the system response at all wavelengths. Experiments with faster time resolution are needed to compare the S_{1R} and $^1p^*$ lifetimes in **2**. However, the kinetic model in Scheme I should explain the difference in fluorescence quantum yields for **1** and **2**, provided all of the rate constants can be estimated (Scheme I). The radiative rate constant, k_f, is obtained from ref 4d. The inverse of the $^1p^*$ appearance time constant[4a] is used as an estimate of k_2, and the $^1p^*$ decay rate constant is approximated by the entries in column 4 of Table I. k_{-2} is obtained from $RT \ln (k_2/k_{-2}) = |\Delta G^\circ|$, where the free energy difference between S_{1R} and $^1p^*$, $|\Delta G^\circ|$, is estimated as 2.5 kcal/mol. For **1**, Φ_f and Φ_s, the fluorescence quantum yields of the fast and slow S_{1R} decays, are predicted to be 0.001 and 0.005, respectively. If $|\Delta G^\circ|$ is 1 kcal/mol larger for **2**, Φ_f and Φ_s are 0.001 and 0.0003, respectively. These estimates qualitatively reproduce the observed trend in the quantum yields, without assuming any change in the $S_{1R} \rightarrow {}^1p^*$ barrier. The explanation for the quantum yield changes based on a decrease in the $S_{1R} \rightarrow {}^1p^*$ barrier cannot explain the nonexponential S_{1R} fluorescence decays.

Interconversion of vertical and twisted arylalkene excited states has been detected in other systems. Equilibration in the triplet manifold for stilbenes and tri- and tetraphenylethylene[9] is well documented, and recently, Saltiel observed a very low quantum yield for emission from excited *trans*-stilbene following excitation of the cis isomer.[10] The low quantum efficiency of this process in stilbenes is due, in part, to the ultrashort lifetime of the intervening twisted state. In **1**, **3**, and **4**, the long $^1p^*$ lifetime and small S_{1R}–$^1p^*$ energy gap (<10 kcal/mol) permit thermal repopulation of and a significant delayed fluorescence quantum yield from S_{1R}. The decreased lifetime and energy of the zwitterionic $^1p^*$ state in **2** significantly reduce the repopulation of S_{1R} and its fluorescence quantum yield.[11] Studies to determine the $^1p^*$ energy in **2** and the solvent- and temperature-dependent quantum yields[14] and lifetimes from S_{1R} in **1**–**4** are currently in progress.

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(11) As an alternative explanation, the red emission could derive from an equilibrium between the $^1p^*$ state and the twisted, excited diradical state.[12] Although the diphenylmethyl radical's fluorescence is centered at 540 nm, the spectrum is structured and significantly narrower than the red emission from TPE.[13] Furthermore, the red emission is seen under conditions where the twisted state is not formed.[4b] Also, the excited diradical state's energy, 89 kcal/mol, obtained from the twisted ground-state energy[6] and the diphenylmethyl radical fluorescence maximum,[13] precludes thermal population of this state from $^1p^*$.

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A Stable Carbene–Alane Adduct

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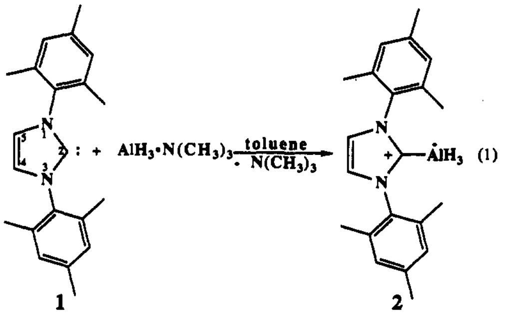
There are no reports of main group III adducts of carbenes. Herein, we report a high-yield synthesis and characterization of a stable compound of this type, 1,3-bis(2,4,6-trimethylphenyl)-imidazol-2-ylidene·AlH_3 (**2**).

Compound **2** was obtained in quantitative yield by treatment of 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene (**1**)[1] with $Me_3N{\cdot}AlH_3$[2] in toluene.[3] Alane adduct **2** is a white solid melting at 246–247 °C. The ^1H NMR spectrum of **2** (THF-d_8) shows a resonance for the $C_{4,5}$ imidazole ring protons at δ 7.42. This is shifted downfield from the corresponding resonance in **1** (δ 7.02).[1] The ^{13}C NMR signal for C_2 of **2** appears at δ 175.3, substantially upfield from the free carbene (δ 219.7).[1] The ^{27}Al NMR resonance of δ 107 for **2** is typical of 4-coordinate aluminum species.[4] These resonances suggest an electronic structure for the imidazole fragment which is intermediate between the free carbene and the fully delocalized imidazolium ion (e.g., **3**).[5]



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