# Stilbenoid Dimers:  Effect of Conjugation Length and Relative Chromophore Orientation

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The unique optical, optoelectronic, and charge conducting properties of stilbenoid compounds and related polymers have found utility in a variety of materials science applications.[1]  These physical properties can be tuned by controlling such variables as conjugation length, alkene stereochemistry (cis or trans), arene regiochemistry (ortho, meta, or para), or substitution of hydrogen atoms with donor and/or acceptor groups.  Chemical variations of this type not only control the molecular electronic structure but also undoubtedly alter the collective interactions between chromophores and therefore modify the solid-state properties.  For example, spectroscopic features characteristic of stilbene aggregates (i.e., blue shifted absorbance and red-shifted emission) are observed in cases where stilbene units have been incorporated into ordered assemblies.[2]  In the case of poly(phenylenevinylene) (PPV) and its derivatives, interchain chromophore−chromophore interactions have been proposed to influence their emissive properties and therefore their response in light-emitting diode applications.[3]

The fate of photoexcitations in a collection of polymer chains remains an outstanding problem in polymer photophysics.  Morphological irregularities, together with poorly defined amorphous regions in the solid, and chain dynamics in solution make these interactions poorly defined.  Additionally, because of facile energy migration, spectroscopic measurements of bulk samples do not reflect the average environment, rather the lowest energy sites.[4]  In solution, interchromophore encounters may lead to multiple collisions and are difficult to probe experimentally.[5]

To understand the effect of bringing two chromophores into close proximity we have designed a family of well-defined organic compounds that hold two chromophores in a precisely determined distance and orientation.  The paracyclophane skeleton serves as the locus of interchromophore contact.  This molecular fragment was chosen because it enforces a cofacial overlap of two phenyl rings and because it minimizes intramolecular motion.  This communication reports the synthesis and full characterization of the molecules shown in Scheme 1, together with a comparison of their optical properties in solution relative to monomeric analogues.

Pseudo-*p*- and pseudo-*o*-dibromoparacyclophane[6] are each reacted with styrene or 4,4′-*tert*-butylvinylstilbene under Heck coupling conditions[7] to give dimers **1a,b** and **2a,b**, respectively.[8]

Compounds **a** and **b** (for **1** or **2**) are configurational isomers, differing in the relative orientation of the pendent groups (i.e., 180° vs 60°).  Single-crystal X-ray diffraction experiments for

## Scheme 1
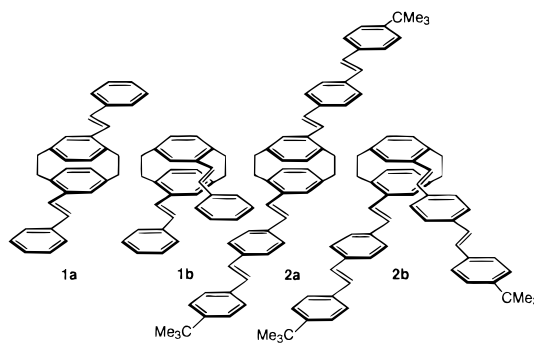


**1a** and **1b** (Figure 1) determine how this geometric relationship influences the overall molecular structure.  Metrical data describing the cyclophane core of **1a** are very similar to published values for other pseudo-para disubstituted cyclophanes.[9]  The characteristic puckering of the [2.2]paracyclophane core can be appreciated by comparing the nonbonded C−C distance between the ipso carbons, C2 and C5A (2.759(2) Å), with the mean separation of planes defined by carbons C1, C3, C4, and C6 (3.070(2) Å).

Two independent molecules, with different torsion angles on the styrene arms, are observed for **1b**.  Torsional distortions in stilbenes are characterized by a relatively flat potential energy surface,[10] and therefore the differences between the two molecules are likely a result of lattice constraints.  Relative to **1a** the structure of **1b** contains a paracyclophane core with a larger inter-ring torsion angle (C1−C7−C8−C9 = 22° for **1b** vs C2−C7−C8A−C5A of 8.5° for **1a**).  Other than puckering of the cyclophane arene, the bond lengths and angles which define the *trans*-stilbene unit in **1a** and **1b** are similar to *trans*-stilbene itself.[10]

The photooptical properties of **1a**, **1b**, **2a**, and **2b** as well as those of the parent chromophores 2,5-dimethylstilbene (**1c**) and 4-(2,5-dimethylstyryl)-4′-*tert*-butylstilbene (**2c**) are shown in
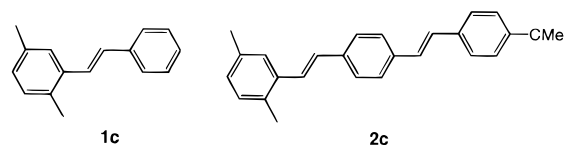


Figure 2.  A slight red shift of 13 nm is observed in the absorbance spectrum of **1a** relative to **1c**.  More pronounced differences are evident in their respective emission spectra ($\lambda_{emis}$(**1a**) = 412 nm vs $\lambda_{emis}$(**1c**) = 355 nm).  Whereas **1c** reveals vibronic definition, the broad band shape (which is maintained down to 77 K) and larger Stokes shift for **1a** mimics that of excimers.[11]  The emission of **1b** is similar to that of **1a**.  However, the close proximity of the two alkene units in **1b** (e.g., C18···C26 = 3.819 Å) results in an apparent splitting of the absorbance band ($\lambda_{abs}$ = 264 and 325 nm) relative to **1c**.  Therefore, unlike an excimer, there is a ground-state electronic interaction between the subunits of **1b**.

The absorbance and emission spectra of **2c** are characteristic of the distyrylbenzene chromophore.  This molecule represents

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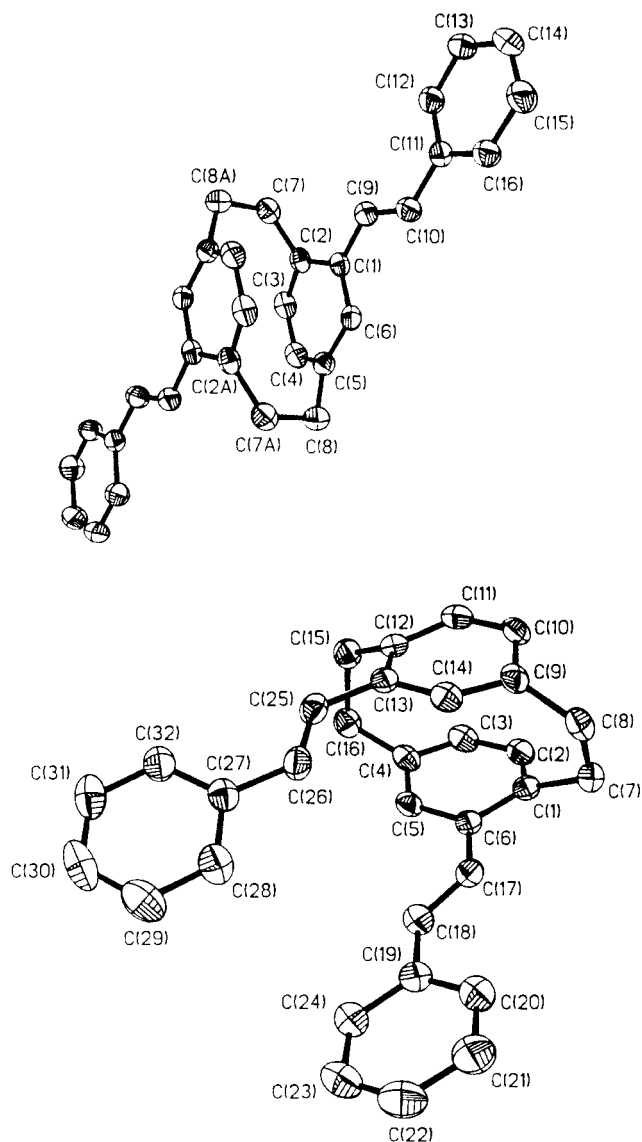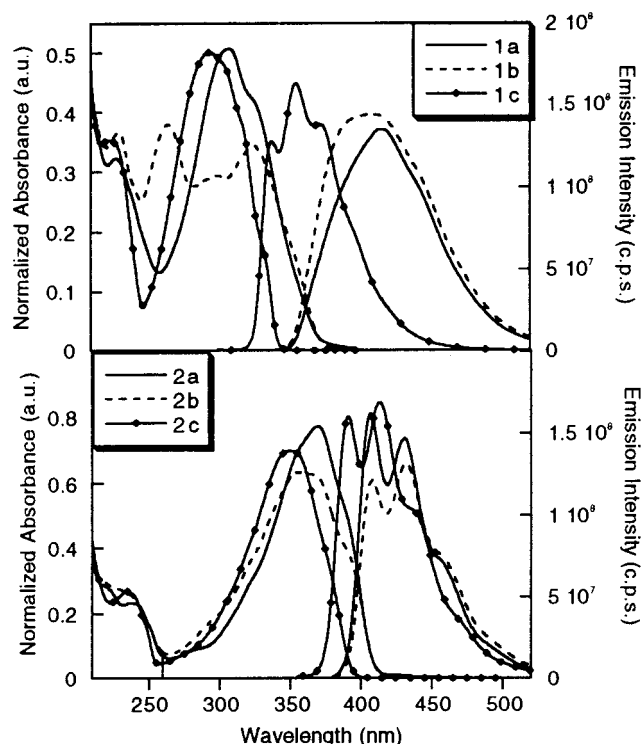
**Figure 1.** ORTEP views of **1a** (top) and **1b** (bottom), showing the atom numbering scheme. Hydrogen atoms were omitted for clarity.



**Figure 2.** Absorption and emission data for compounds **1a**−**c** and **2a**−**c**. All measurements were made using degassed hexane as solvent. Emission spectra were measured by exciting at the absorption maxima.

a small oligomeric unit from a PPV chain. A red shift of ca. 15 nm is observed in the absorbance of the "dimers" **2a** and **2b** relative to **2c**. Note that unlike **1a** and **1b**, the absorbance spectra of **2a** and **2b** are similar. Likewise, the emission data from **2a** and **2b** are indistinguishable (16 nm red-shifted from that of **2c**), and vibronic structure is observed.

The remarkable difference in spectroscopic properties between **1a,b** and **1c** can be understood in terms of excitation transfer[12] between the excited stilbene chromophore of **1a,b** and a lower energy inter-ring excited state containing the [2.2]cyclophane core.[13] The highest energy vibrational band (0,0 transition) in the emission spectrum of **1c** (338 nm = 29 600 cm$^{-1}$) gives a good estimate of the excited-state energy of the stilbene arm of **1a,b**. For the corresponding energy of the "through-space" paracyclophane state we note the energies of the blue edge of the broad emission bands of [2.2]paracyclophane (330 nm = 30 300 cm$^{-1}$), divinyl[2.2]paracyclophane[14] (360 nm = 27 800 cm$^{-1}$), and **1a,b** (365 nm = 27 400 cm$^{-1}$). This trend indicates that the state containing the cyclophane core is lower in energy than that

of the styryl chromophore and that this state is delocalized to some extent over the entire molecule. A similar excitation transfer appears to be energetically unfavorable in the case of **2a,b** because the excited-state energy of the distyrylbenzene chromophore (0,0 transition of **2c**: 391 nm = 25 600 cm$^{-1}$) is lowest in energy. Thus, no "excimer-like" emission is observed for **2a,b**.

In summary, we have shown that the paracyclophane framework can be used to constrain chromophores of differing chain lengths at specified distances and geometries. For dimers containing stilbene chromophores, the absorbance data show strong ground state electronic coupling, while the broad featureless emission suggests delocalization of the excited state from the isolated stilbene component. These observations imply that through space delocalization across the transannular gap leads to a more stable excited state than the isolated stilbene fragment and that this is the emissive state. Holding larger chromophores (e.g., distyrylbenzene) in close proximity results in negligible ground state interactions and in emission spectra that closely resemble the parent chromophore. Further, the vibronic definition of the emission spectra of **2a,b** implies that the excitation is localized to one-half of the "dimer". It seems that for **2a** and **2b** there is no driving force to transfer energy to the "through space" state. Altogether, these observations parallel nicely the behavior of polymers with discrete stilbene units in the backbone such as poly(paracyclophene) (which display red-shifted aggregate emission)[2e] and PPV for which increasing interchain contacts does not affect emission.[15]

**Supporting Information Available:** Complete experimental details for the preparation of all new compounds and for the X-ray crystallographic determination of **2a** and **2b** (23 pages). See any current masthead page for ordering and Internet access instructions.

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