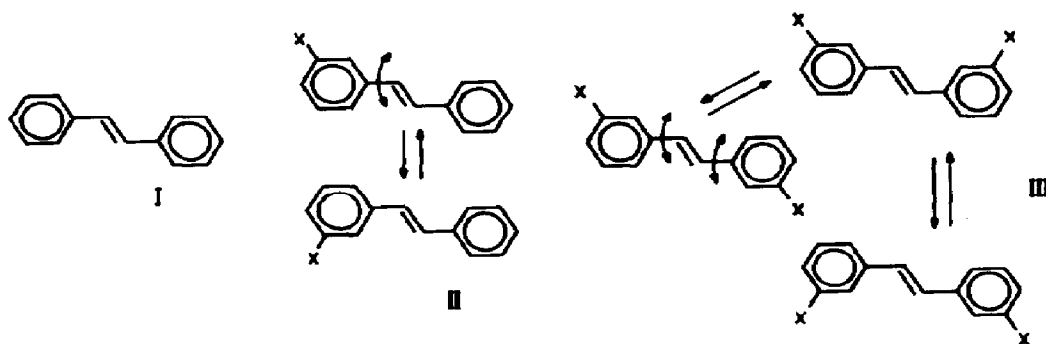


EMISSION-SPECTROSCOPIC EVIDENCE FOR THE EXISTENCE OF GROUND-STATE ROTAMERS IN
TRANS-DIARYLETHYLENES

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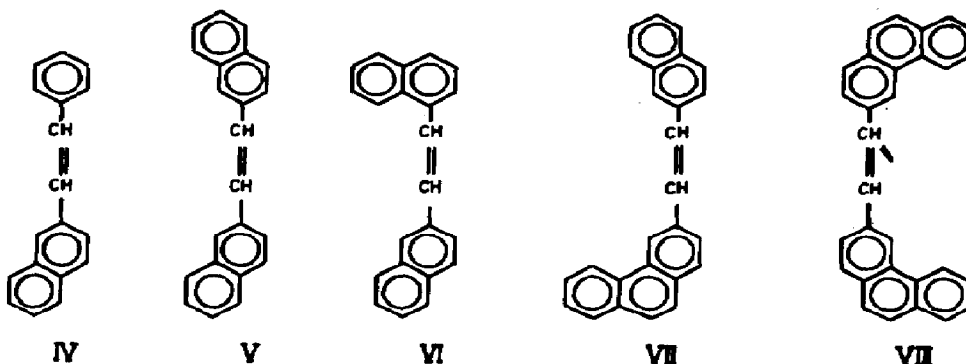
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In the absence of steric repulsion, trans 1,2-diarylethylenes, the simplest one being trans-stilbene, I, tend to assume a resonance-stabilized coplanar configuration.

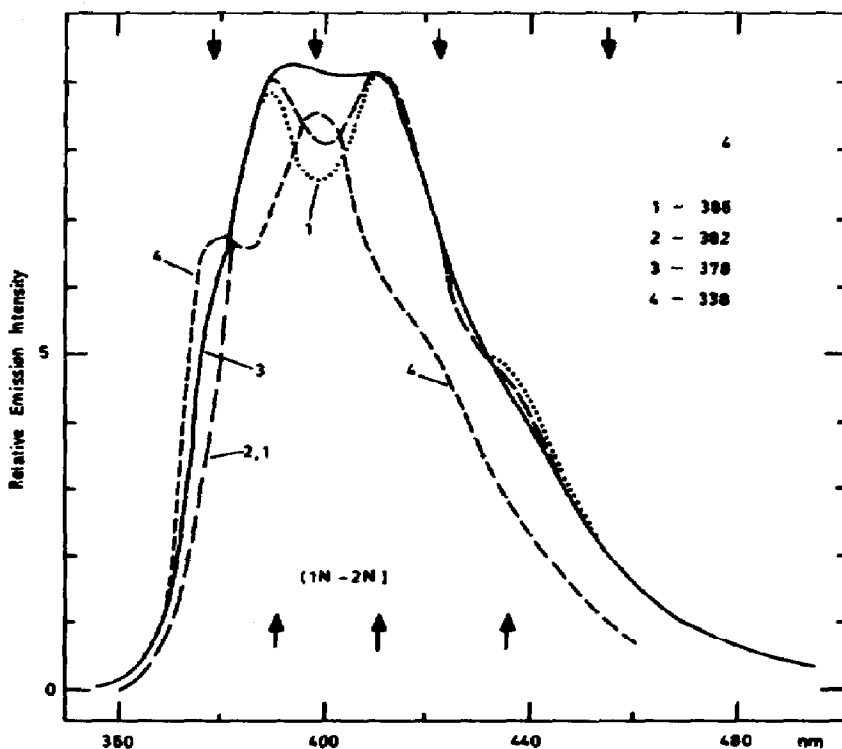


If at least one of the rings in I is substituted at X, rotation around one or both of the quasi-single bonds gives rise to two or three non-identical rotamers, which are approximately isoenergetic and may be expected to exist in solution as an equilibrium mixture. On principle, the rotamers may differ in various physical properties, such as UV, IR, and PMR absorption spectra. However, since the only parameter which can be varied is the temperature, which may affect the equilibrium, identification is inherently difficult. Measurements of emission properties have the advantage of the possibility of observing variations with the wavelength of the exciting light, both regarding the form of the emission spectra and the quantum yields and decay kinetics.

We investigated diarylethylenes of types II and III in which at least one aryl is 2-naphthyl or 3-phenanthryl, e.g. IV-VIII. Emission spectra were measured as a function of exciting wavelength, at ambient and at reduced temperatures. In addition, decay curves were measured at ambient temperature, as a function of the wavelength of both the exciting and the emitted light.



Emission spectra were observed to vary with wavelength of excitation, as shown for VI in the Figure. The emission seems to be a superposition of two sets of peaks, denoted \downarrow and \uparrow in the Figure, with the relative contribution of each set varying with λ_{exc} . Excitation in the long λ tail of the absorption spectrum results in what looks like almost pure \uparrow . The situation is even more clear-cut at reduced temperatures.



Emission spectra of compound VI in methylcyclohexane (ca. 10^{-5} M) excited at the wavelengths indicated, at room temperature.

The fluorescence decay kinetics of IV and V vary with λ_{exc} , and can be expressed only by a bi-exponential function, except when exciting in the long λ tail of the absorption. Thus, for V the two decay times are 2.2 and 7.3 ns, respectively. Again the contribution of each decay changes with λ_{exc} , and also with the part of the emission spectrum being measured. As expected from the two rather different decay rates, partial oxygen-quenching of the emission results in changes in the shape of the emission spectrum, enhancing the contribution of the short-lived component. Again as expected, the fluorescence quantum yield of the short-lived component is 2-3 times smaller than that of the longer-lived one. Competing excited-state reactions, such as trans+cis isomerization or steps preceding it, are probably much more efficient in the species responsible for the short-lived emission.