

plexes. Our results include absolute values for some of the rate constants involved and relative chemiluminescence quantum efficiencies of peroxy radical cross-combinations.

Adiabatic photoreactions in dilute solutions of *p*-substituted *N,N*-dialkylanilines and related donor-acceptor compounds

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Twisted intramolecular charge transfer (TICT) stable excited states can occur in molecules in which two chromophores are separated by one (twisted) single bond. The TICT state is achieved after absorption to the lowest-lying Franck-Condon excited state of that molecule by an adiabatic photoreaction. This lower-lying TICT state potential minimum in the hypersurface of the lowest-lying excited state of the total π electronic system comes from higher-lying excited states in the ground state molecular geometry and gives rise to the effect of dual fluorescence which allows us to study the kinetics of the twist mechanism. If the *para* substituent to the *N,N*-dialkylaniline is large (9-anthryl or sulphone) the aniline twists around that substituent, but if the substituent is small (nitrile) or flexible (ester) the dialkylamino group twists around its phenyl ring. The population of the TICT state is favoured by (1) the dialkylamino group ionization potential, (2) the substituent electron affinity, (3) the lifetime of the excited state, (4) its dipole-dipole interaction with the solvent and (5) a low viscosity.

Triplet excimer formation with phenanthrene: the importance or relative chromophore configuration

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Triplet excimers were detected in dilute solution with 1,3-di(9-phenanthryl)propane (99P3P) by triplet-triplet (T-T) absorption spectroscopy in the nanosecond time domain. From an analysis of the T-T absorption spectra as a function of time, the kinetics of the intramolecular triplet excimer formation were resolved as a function of temperature and solvent viscosity. For the triplet excimer

a lifetime of 420 ns (at 20 °C in methylcyclohexane) and a stabilization energy of 9 kJ mol⁻¹ resulted.

With the asymmetrically substituted diphenanthrylpropanes 29P3P and 39P3P, a triplet excimer could not be detected. This dependence of triplet excimer formation on the relative configuration of the phenanthrene moieties supports the assumption that with 99P3P the main contribution to the stabilization of the excimer comes from dispersion forces. This is in accord with recent theoretical considerations.

Also, singlet excimers are formed with 99P3P and decay predominantly by internal conversion. Their kinetics were studied using time-correlated single-photon counting.

Nature of the low temperature emission from 9-nitroanthracene

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From previous studies in this laboratory we have reported the phosphorescence behavior of nitronaphthalenes and the lack of phosphorescence from nitrobenzene. For 9-nitroanthracene (9-NA) where the lowest triplet is a π, π^* triplet, published reports indicate a phosphorescence with a 0-0 band in the vicinity of 20 000 cm⁻¹, which is somewhat inconsistent with the $S_0 \rightarrow T_1$ transition of 9-NA at 14 630 cm⁻¹, deduced by oxygen perturbation techniques. We undertook an investigation of the luminescence behavior of this molecule with the additional feature that the formation of an electron donor-acceptor complex was employed to assist in identifying the emission observed at 77 K. The advantage in forming a complex is that 9-NA becomes stabilized. Our results indicate that, in fact, the emission at 77 K from 9-NA is not molecular phosphorescence but emanates from the photoproduct of an efficient photochemical event. The quantum yield for the disappearance of 9-NA in ethyl alcohol at 77 K appears to approach unity. Elucidation of this photochemical event and the effect of solvent and temperature on the UV excitation behavior of 9-NA are discussed.