

is shown to be incorrect. A general mechanism for BP photopinacolization is proposed. It may also be noted that measurements at low light intensities (*e.g.* quantum yield determinations) and at high light intensities (*e.g.* flash photolysis) in a given system may be probing different mechanisms.

### **Time-resolved spectroscopy and chemical reactivity of energetic transient species of nitroaromatics**

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Electronic excitation of trinitrobenzene (s-TNB) leads to a charge transfer complex between deprotonated s-TNB and molecular oxygen. Electronic excitation of trinitrotoluene (s-TNT) generates an *aci*-quinoid transient in non-polar solvents. In the gas phase, electronic excitation of s-TNT forms the 2,4,6-trinitrobenzyl radical. This species is also formed from electronically excited s-TNT, 2,4,6-trinitrobenzyl chloride and hexanitrobibenzyl in 1,4-dioxane at room temperature and in ether–isopentane–ethanol at 77 K. Nanosecond laser spectroscopy and kinetic studies of nitronaphthalenes indicate that the triplet states of these molecules behave like  $\eta, \pi^*$  states in non-polar solvents while in polar solvents the  $\eta, \pi^*$  character is reduced with a simultaneous increase in the charge transfer character of the states. Because of the symmetry of nitro substitution, the triplet state of 1,4-dinitronaphthalene remains  $\eta, \pi^*$  even in polar solvents.

### **Magnetic field effect on triplet sublevel relaxation: a novel method to probe the dynamics of short-lived triplet intermediates in photoreactions**

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A mechanism is described whereby the influence of an external magnetic field on the relaxation between the sublevels of an electronically excited triplet state, which is subject to sublevel-selective deactivation, modulates the yield of photochemical products originating from such a triplet intermediate. A theory of this novel magnetic field effect is outlined and its first experimental application to determine the absolute decay constants of short-lived triplet exciplexes be-

tween dye triplets and halogen anilines is reported. The magnetic field effect on the yield of free radicals in these systems represents the first direct experimental evidence for sublevel-selective depopulation of triplet states in fluid solution at room temperature.

The mechanism described may induce magnetic field effects on any triplet reaction competing with sublevel-selective deactivation and can thus provide the basis of a general method to study the dynamics of short-lived triplet intermediates.

### **Kinetics of triplet sublevel selective photochemical reactions in the solid state**

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A detailed description of the overall kinetics of photochemical reactions must deal with photophysical activation and deactivation rates as well as with true photochemical rates. On the basis of the hypothesis that the chemical reaction rates of the individual triplet zero field levels have different values for photoreactions involving the lowest excited triplet state, a method is presented for the evaluation of these rates from bulk measurements under steady state illumination conditions. The complications arising from the detection of solid state reactions are discussed, and a simple solution is given, illustrated by a numerical example.

### **Observation of triplet states of stilbene and related compounds in solution and analysis of the decay mechanism**

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Transients formed by energy transfer from triplet donors to stilbenes and arylethylenes are observed in the 360 - 400 nm region by nanosecond laser pulse excitation. The transients (lifetimes in the 100 ns range) are assigned to the lowest triplet state of the arylethylenes rather than to 1,4-biradicals or exciplexes. From spectroscopic and kinetic results, including those from rigid model compounds of stilbene as a comparison, it is suggested that the triplet absorption