

originates from the *trans* configuration  $^3t^*$  of the arylethylenes. The twisted configuration  $^3p^*$ , which decays into the *trans* and *cis* forms, is in rapid equilibrium with  $^3t^*$ . The effects of substitution, temperature, solvent and quenchers (azulene and oxygen) on the decay of the  $^3t^* \rightleftharpoons ^3p^*$  triplet equilibrium are presented and discussed.

### **Energy transfer and photochemical changes in molecular crystals**

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The rise and decay of the prompt fluorescence from pure and doped anthracene crystals at low temperatures in the 100 ps to 10 ns time range allows the study of excitation energy transfer from the host lattice to guest impurity sites and between different sites occupied by the impurity. For 2-hydroxyanthracene (2-OHA) as the impurity, irradiation of the crystals at elevated temperatures ( $T > 200$  K) leads to a photochemical change resulting in heterodimer formation at one of the impurity sites ( $O_9$ ). A study of the crystals before and after photodimerization allows us to investigate the details of the photochemical change and the roles played by X traps and other structural defects. The experimental arrangement involving a picosecond laser system is briefly described and the results are discussed.

### **Kinetic and mechanistic aspects of the photoinduced $OCH_3$ substitution in 3,5-dinitroanisole**

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Nucleophiles (N) such as triethylamine and  $OH^-$  react with the lowest triplet state of 3,5-dinitroanisole (3,5-DINA) in mixed aqueous solvents, yielding 3,5-dinitrophenolate. In mixed aqueous solvents the primary excited state, prepared by excitation at 353 nm, forms a hydrogen bond prior to intersystem crossing. The hydrogen-bonded triplet state is involved in three parallel reactions with N, producing an exciplex E and two  $\sigma$  complexes with either a C(2)-N or a C(4)-N bond. The latter complexes revert to 3,5-DINA. Bonding in the E involves lone pair electrons on  $OCH_3$  and N. It branches into a more stable exci-