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<p>Two studies are described. The first involved the use of time resolved electron spin resonance as a mechanistic and spectroscopic probe of two fundamental reactions of ketone photochemistry: intermolecular hydrogen abstraction by the triplet state of benzophenone and triplet state alpha-cleavage of 1,3-diphenylacetone (dibenzyl ketone). It was found that the forces restricting the ground state conformations of these ketones also restrict the triplet state conformations. The second study used steady-state spectroscopies and laser flash photolysis techniques to define the mechanism involved in biologically and medically related compounds employed as anticancer agents and a compound called A2-E, a bis-retinoid found in ocular cells, believed to be associated with age-related macular degeneration.</p>				
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FINAL TECHNICAL REPORT

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prepared by

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Two students were supported by the AASERT grant:

Mr. Matthew Lipson (6/1/93 to 8/30/94)

Ms. Ariella Evenzahav (9/1/94 to 2/28/97).

Mr. Lipson received the Ph.D. degree in October 1994; the title of his thesis is: "Conformational Control of the Photochemistry and Photophysics of Benzophenone and Diphenylacetone".

The following is a summary of his thesis research:

Time resolved electron spin resonance was used as a mechanistic and spectroscopic probe of two fundamental reactions of ketone photochemistry: intermolecular hydrogen abstraction by the triplet state of benzophenone and triplet state α -cleavage of 1,3-diphenylacetone (dibenzyl ketone).

Studies on 4,4'-dimethylbenzophenone and a family of α -oxo[1.n] paracyclophanes (cyclophanobenzophenone, $n=8-12$) were made. Molecular mechanics show that as the methylene tether connecting the two phenyl rings of these paracyclophanes is shortened, the two phenyl rings rotate out of conjugation with the carbonyl π system, and the C-C-C bond angle at the carbonyl carbon shrinks from ca. 120° for cyclophanobenzophenone₁₂ to ca. 109° for cyclophanobenzophenone₈. These changes in ground state conformation manifest themselves in the properties of the corresponding triplet states as a gradual decrease in both the rate of hydrogen abstraction and the zero field splitting.

It was found that the forces restricting the ground state conformations of these ketones also restrict the triplet state conformations. As the conformation of the triplet state changes from $n=12$ to $n=8$, unpaired electron density in the triplet state migrates from the oxygen n orbital to the phenyl π systems.

Observation was made of the lowest triplet states of dibenzylketone and two methylated derivatives by time-resolved electron spin resonance at 15K in methylcyclohexane glass. The spectral features were found to be broad with multiple peaks in the $\Delta M_S=2$ region, which were assigned to a multitude of conformations frozen into the glass. Successive experiments on a single sample provided evidence that certain of these conformations could be photochemically removed. Zero field splitting parameters, triplet sublevel populating rates, and rate of triplet state α -cleavage were found to be more

sensitive functions of conformation than would have been expected for nominally aliphatic ketones.

It was concluded that a significant portion of the unpaired electron density of the triplet state of dibenzylketone and its derivatives is delocalized into the phenyl rings; furthermore, it is proposed that this delocalization is responsible for the previously observed change in rate of triplet state α -cleavage with substitution in the phenyl rings.

Publications of Mr. Lipson:

1. C.-H. Wu, W.S. Jenks, I.V. Koptug, N.D. Ghatlia, M. Lipson, V.F. Tarasov, and N.J. Turro, "Time-Resolved ESR Examination of a Simple Supramolecular Guest-Host System. Electron Spin Exchange Interaction in Micellized Spin-Correlated Radical Pairs," *J. Am. Chem. Soc.*, **115**, 9583 (1993).
2. M. Lipson, P.F. McGarry, I.V. Koptug, H.A. Staab, N.J. Turro, and D.C. Doetschman, "Electron Spin Resonance of the Lowest Excited Triplet States of α -Oxo[1.n]paracyclophanes [Cyclophanobenzophenones]. Effect of Molecular Geometry on the Electronic Character of the Triplet State," *J. Phys. Chem.*, **98**, 7504 (1994).
3. M. Lipson, T.H. Noh, C.E. doubleday, J.M. Zaleski, and N.J. Turro, "Conformational Control of the Photochemistry and Photophysics of Diphenylacetone," *J. Phys. Chem.*, **98**, 8844 (1994).
4. M. Lipson and N.J. Turro, "Picosecond Investigation of the Effect of Solvent on the Photochemistry of Benzoin," *J. Photochem. Photobiol. A: Chem.*, **99**, 93 (1996).

Ms. Evenzahav completed her research for the Ph.D. degree and will defend her thesis on July 7, 1997. The title of her thesis is,
"Viewing Biologically Significant Systems through a Photochemical Looking Glass: Part 1. Novel Photoarrangement of Eneidyne
Part 2. Photophysical Investigation of a Compound Associated with Macular Degeneration."

The following is the Abstract from her Ph.D. thesis.

The photochemistry and photophysics of biologically and medically related compounds employed as anticancer agents, and a compound found in ocular cells believed to be associated with vision disorder were examined. Eneidyne compounds are rendered potent antitumor agents by applying the Bergman rearrangement to yield a cyclized product via an aromatic biradical. It was shown that a series of eneidyne molecules are photochemically

reactive to yield a product expected from a thermal Bergman rearrangement reaction. Depending on the substituents on the triple bonds, triple bond photoreduction products can also be obtained. The product distribution is rationalized by proposing that a different mechanism yields each class of products; the Bergman-type product forms via an aromatic biradical, identical in structure to that expected from the thermal case, and can be a product of both the singlet and triplet excited states of the enediynes. The photoreduction products result from excitation of one triple bond, and form from the triplet state of the enediyne. Both steady-state spectroscopies and laser flash photolysis techniques are used to define these mechanisms.

A2-E is a bis-retinoid found in ocular cells where the two polyene moieties are connected via a pyridinium ring. A2-E has been shown to be connected to age-related macular degeneration, a disease of the eye. Steady state and time resolved spectroscopic techniques were employed to examine the photophysical and photochemical properties of the compound. It was found that the photochemical behavior of this species is very similar to that of its parent compound, retinal, and does not display characteristics typical of pyridinium photochemistry. In homogeneous environments, A2-E may provide helpful information in understanding the action of A2-E within a cellular environment.

Publications of Ms. Evenzahav:

1. N.J. Turro, A. Evenzahav, and K.C. Nicolaou, "Photochemical Analogue of the Bergman Cycloaromatization Reaction," *Tetrahedron Letts.*, **35**, 8089 (1994).
2. C. Turro, A. Evenzahav, S.H. Bossmann, J.K. Barton, and N.J. Turro, "Excited State Properties of $\text{Rh}(\text{phi})_2(\text{phen})^{3+}$ and Related Complexes: A Strong Photooxidant," *Inorg. Chim. Acta*, **243**, 101 (1996).
3. A. Evenzahav and N.J. Turro, "Photochemical Rearrangement of Eneidyne: Is a 'Photo-Bergman' Cyclization a Possibility?", *J. Am. Chem. Soc.*, submitted.