

Investigating the Photochromism of the Dimethyldihdropyrene System

**R. Scott Murphy, Y. Chen,
Reginald H. Mitchell and Cornelia Bohne**

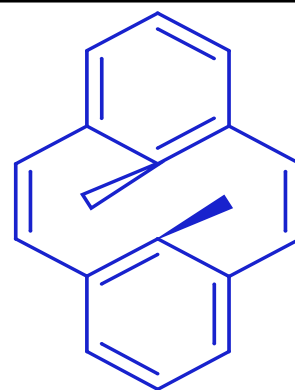
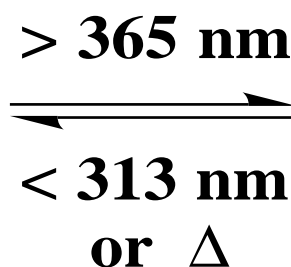
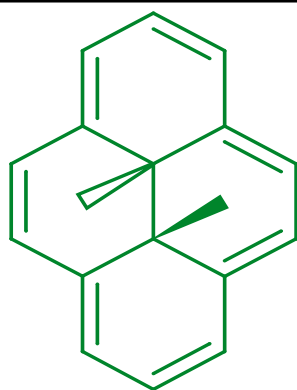
**University of Victoria
P.O. Box 3065
Victoria, B.C.
CANADA
V8W 3V6**

email: srmurphy@uvic.ca



Photochromism

...is a reversible transformation by which a single chemical species is induced in one or both directions by electromagnetic radiation between two states having distinguishable absorption spectra.



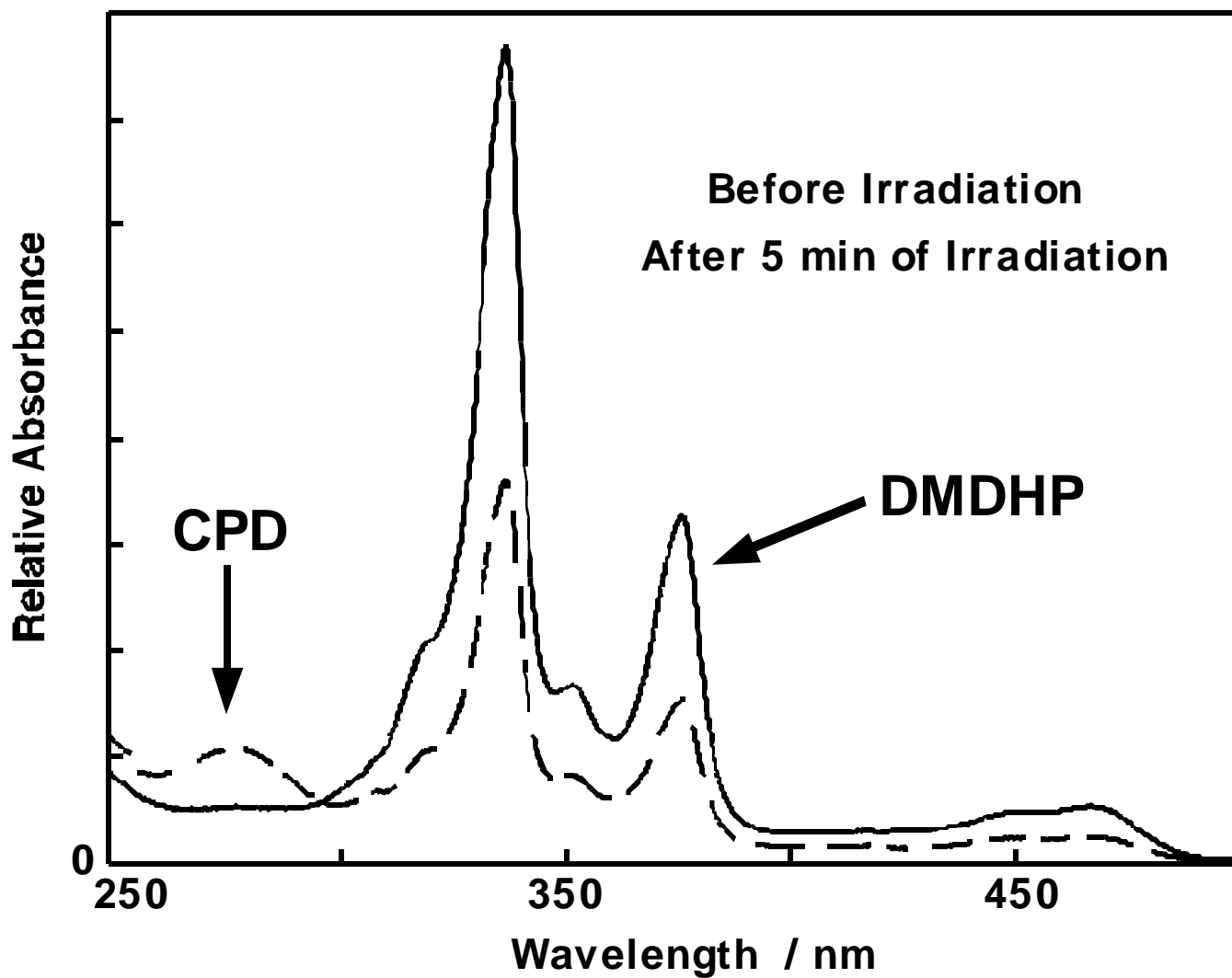
Dimethyldihydropyrene

Cyclophanediene

**DMDHP is
3.45 kcal/mol
more stable than CPD**

(Schmidt, W. *Helv. Chim. Acta* **1971**, 54(3), 862)

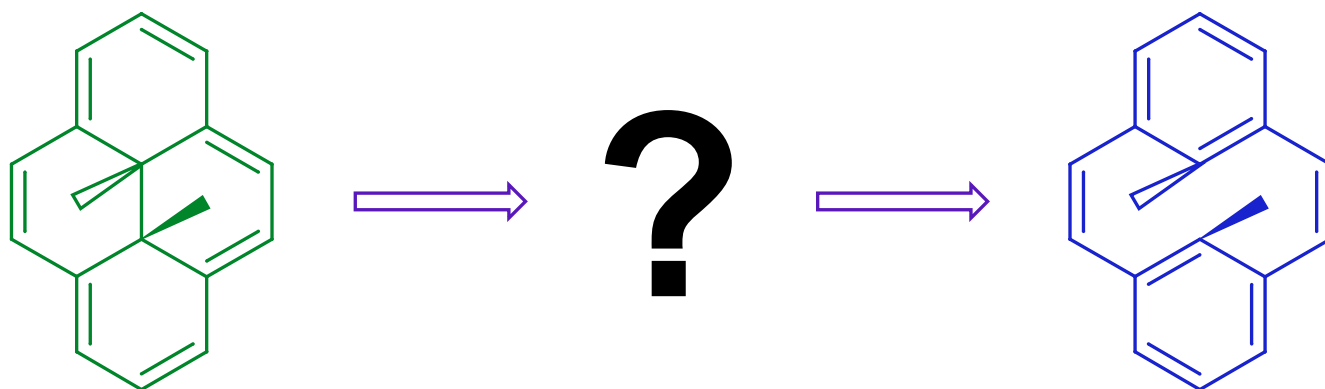
DMDHP Photolysis



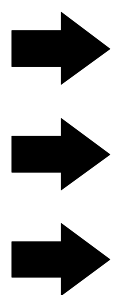
$$\Phi_{1 \rightarrow 2} = 0.02 \quad \Phi_{2 \rightarrow 1} = 1.0$$

(Schmidt, W. *Helv. Chim. Acta* **1971**, 54(3), 862)

Transient Determination



?

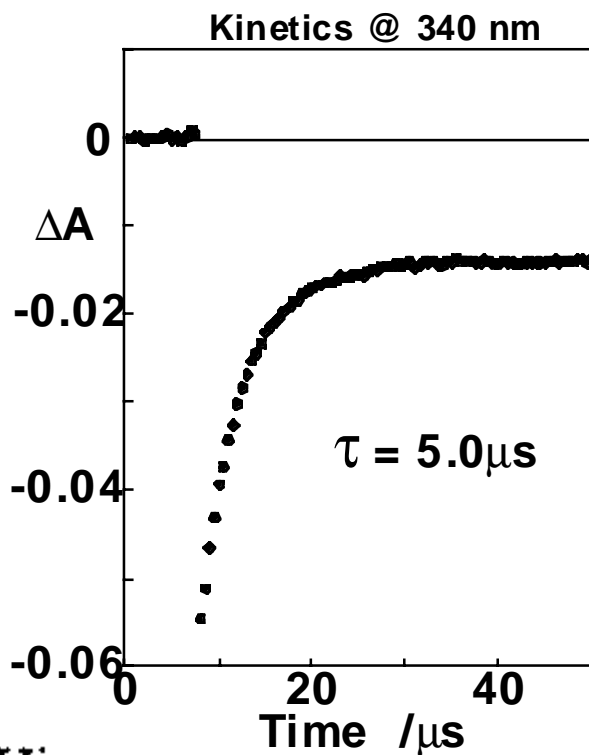
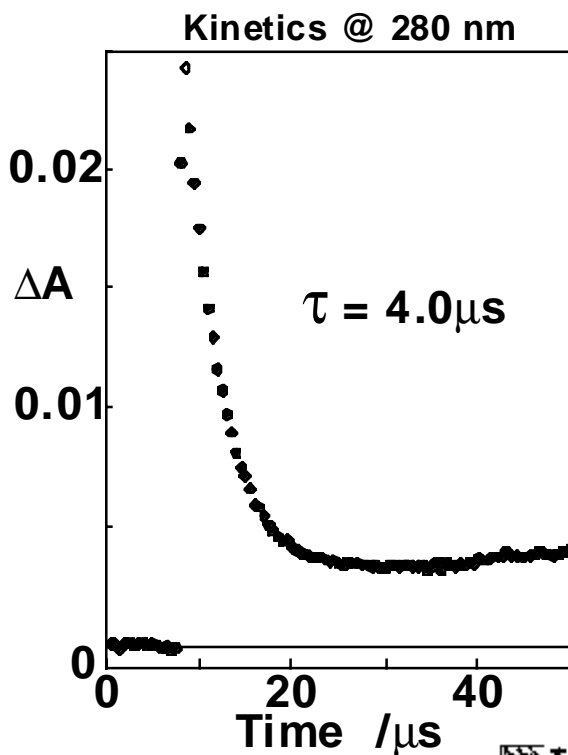
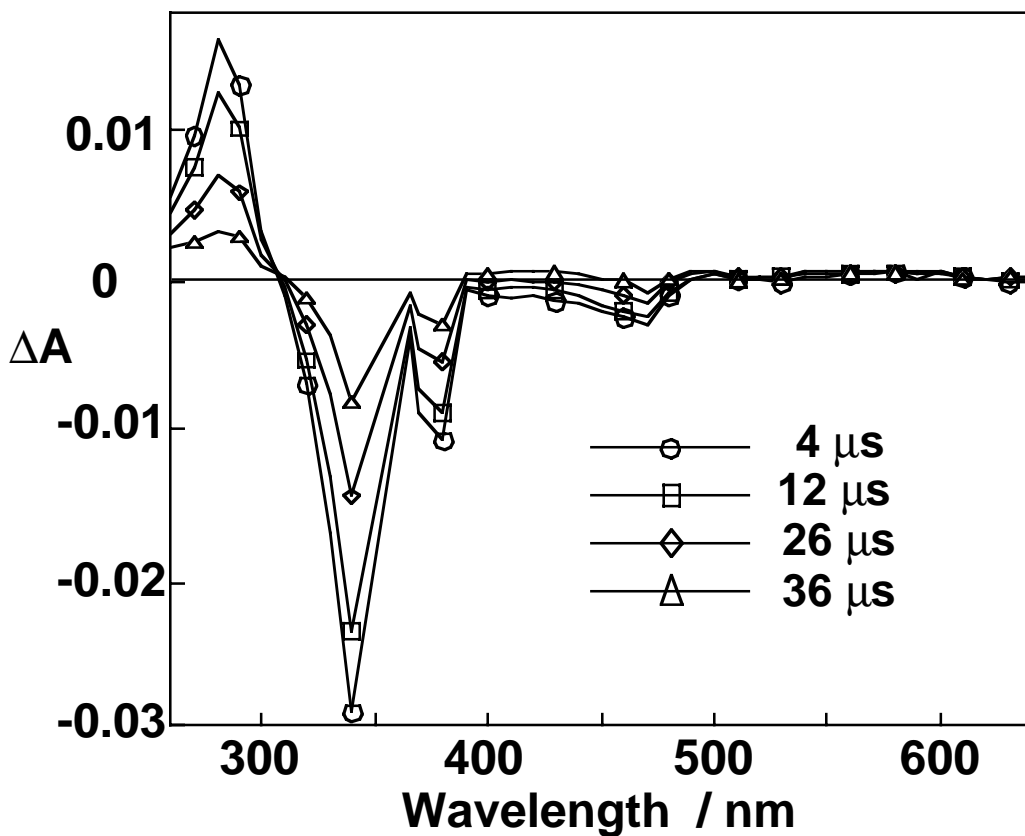


Singlet Excited State

Triplet Excited State

Triplet Biradical

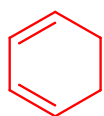
Transient Absorption Spectra



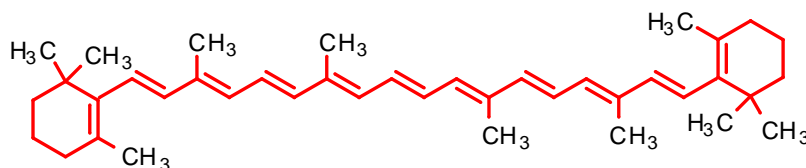
The Quenching Methodology

O₂

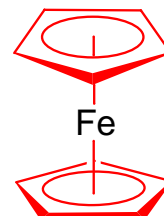
Triplet Quenchers



1,3-CHD

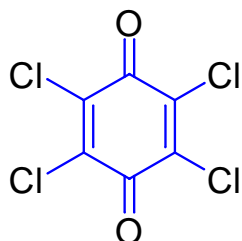


β-Carotene

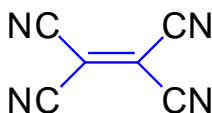


Ferrocene

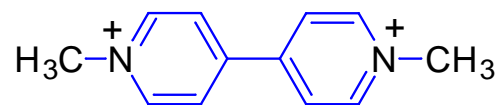
Electron Acceptors



Chloranil

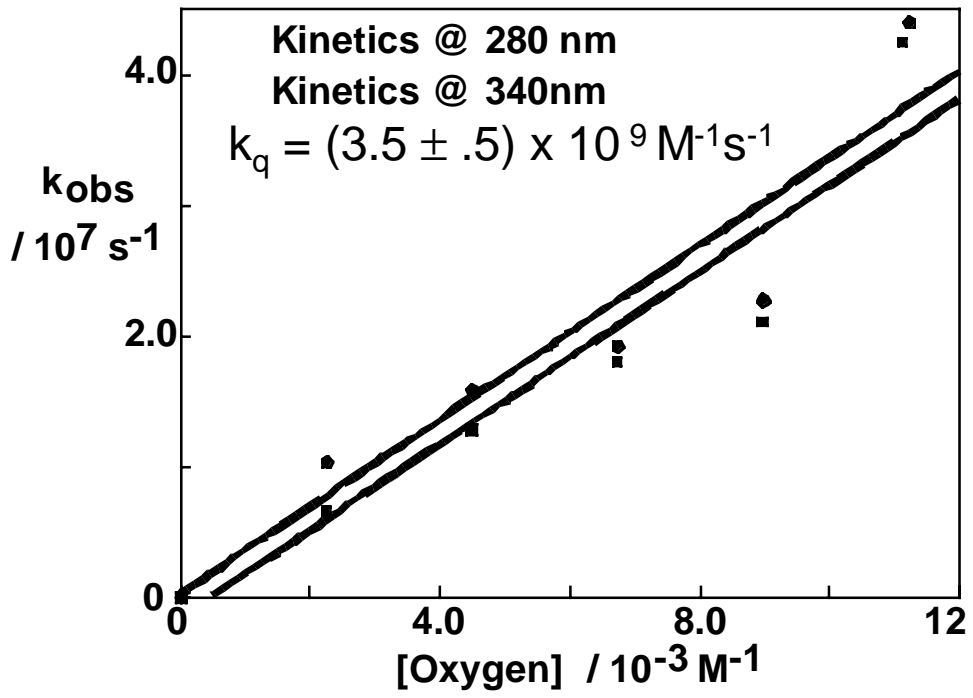
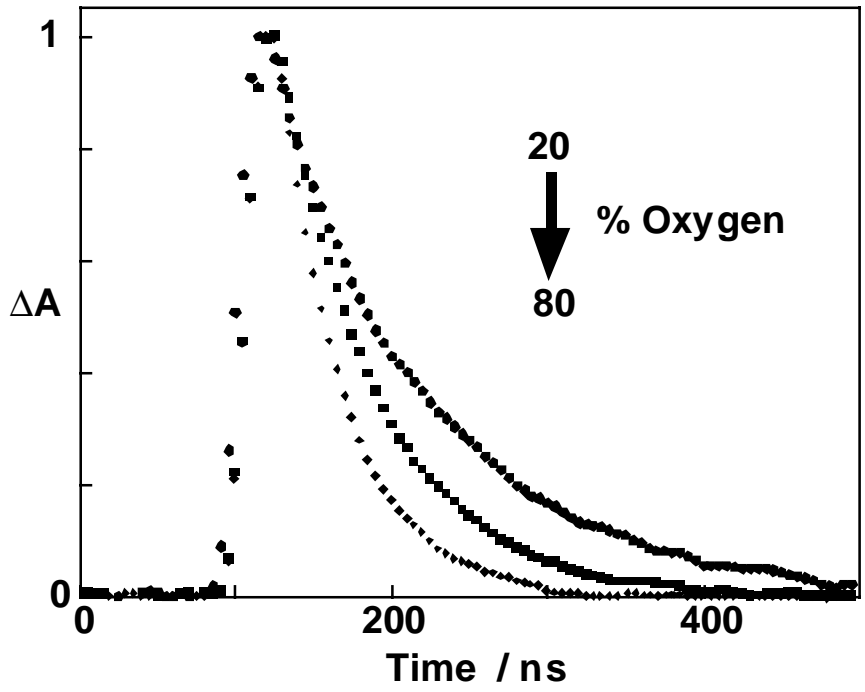


Tetracyanoethylene

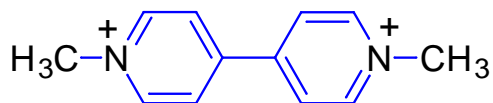


Methyl Viologen

Oxygen Quenching

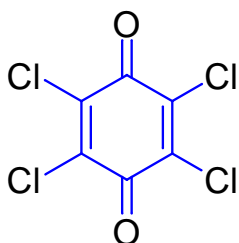


The Electron Acceptors



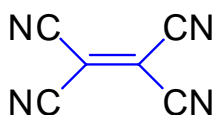
Methyl Viologen

**No Growth for the Radical Cation
was Observed @ 603 nm**



Chloranil

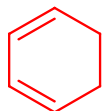
**A Growth was Observed at 280 nm
but it was due to Triplet Chloranil**



Tetracyanoethylene

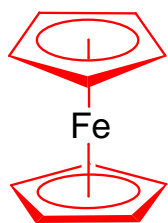
**Quenching was Observed but
TCE also Absorbs. No Radical
Anion was Observed**

The Triplet Quenchers



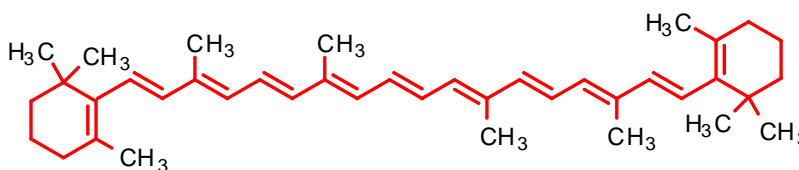
The ΔA was Quenched but not the Lifetimes. Possible Static Component

1,3-CHD



No Observable Quenching

Ferrocene

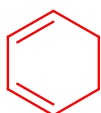


β -Carotene

A Growth was Observed at 520 nm!!

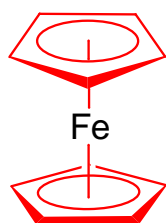
Low-Lying Triplet!

E_T / kcal mol⁻¹



1,3-CHD

52

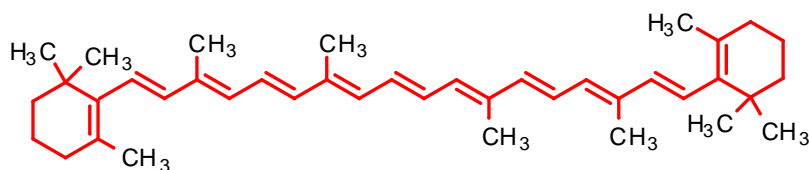


Ferrocene

38

O₂

22

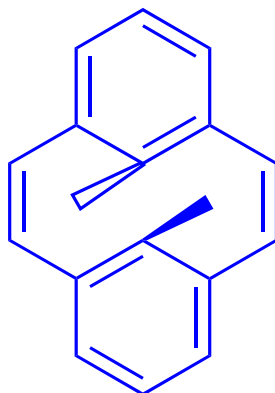


β-Carotene

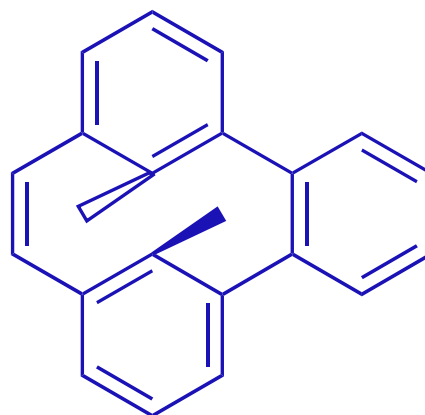
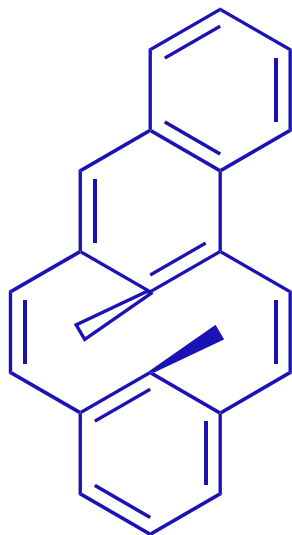
21

(Murov, S.L. *et. al Handbook of Photochemistry* 2nd ed. **1993**)

Future Goals



Study the Reverse Process!



The Benzo[a]- and Benzo[e]- Isomers!

Acknowledgments

NSERC - Canada

University of Victoria

