AD-A199 206

DTIC FILE COPY (4)

REPORT DOCUMENTATION PAGE

1b RESTRICTIVE MARKINGS	
2b DECLASSIFICATION / DOWNGRADING SCHEDULE	3 DISTRIBUTION / AVAILABILITY OF REPORT Approved for public release. Distribution unlimited.
4 PERFORMING ORGANIZATION REPORT NUMBER(S) Technical Report No. 2	5 MONITORING ORGANIZATION REPORT NUMBER(S) Office of Naval Research
6a NAME OF PERFORMING ORGANIZATION University of Massachusetts — 6b OFFICE SYMBOL (If applicable)	7a NAME OF MONITORING ORGANIZATION Office of Naval Research
6c ADDRESS (City, State, and ZIP Code) Dept. of Chemistry Univ. of Massachusetts Amherst, MA 01003	7b ADDRESS (City, State, and ZIP Code) 800 N. Quincy Street Arlington, VA 22217
8a NAME OF FUNDING / SPONSORING ORGANIZATION Office of Naval Research — 8b OFFICE SYMBOL (If applicable)	9 PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER N00014-87-K-0464
8c ADDRESS (City, State, and ZIP Code) 800 N. Quincy St. Arlington, VA 22217	10 SOURCE OF FUNDING NUMBERS PROGRAM ELEMENT NO / PROJECT NO / TASK NO / WORK UNIT ACCESSION NO

11 TITLE (Include Security Classification)

Non-Kekulé Molecules - Theory, Practice and Uses

12 PERSONAL AUTHOR(S)

Paul M. Lahti, Andrew Ichimura, David Modarelli, Mark Kearley

13a. TYPE OF REPORT	13b. TIME COVERED	14. DATE OF REPORT (Year, Month, Day)	15. PAGE COUNT
Technical	FROM 6/1/88 TO 8/31/88	1988 June 22	11

16 SUPPLEMENTARY NOTATION

17 COSATI CODES			18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)
FIELD	GROUP	SUB-GROUP	

19. ABSTRACT (Continue on reverse if necessary and identify by block number)

INDO-CI and AM1-CI semiempirical computations both give results in good agreement with qualitative theoretical expectations for organic polyradicals, as well as diradicaloid species related to tetramethylene ethane. Phenoxyradicals linked through conjugation should be experimentally accessible models for organic super paramagnetic species. Peroxyoxalate esters are useful thermal and photochemical phenoxy precursors which are fairly stable at room temperature, but photochemically and thermally (> 70°C) labile.

20 DISTRIBUTION / AVAILABILITY OF ABSTRACT ☒ UNCLASSIFIED/UNLIMITED ☐ SAME AS RPT ☐ DTIC USERS	21 ABSTRACT SECURITY CLASSIFICATION Unclassified
22a NAME OF RESPONSIBLE INDIVIDUAL Dr. Kenneth Wynne	22b TELEPHONE (Include Area Code) (202) 9696-4409 — 22c OFFICE SYMBOL

DD FORM 1473, 84 MAR — 83 APR edition may be used until exhausted. All other editions are obsolete.

SECURITY CLASSIFICATION OF THIS PAGE

88 9

OFFICE OF NAVAL RESEARCH

Contract # N00014-87-K-0464

R&T Code 413c037

Technical Report #2

NON-KEKULE MOLECULES -- THEORY, PRACTICE, AND USES

by

Paul M. Lahti, Andrew Ichimura,
David Modarelli, Mark Kearley

Prepared for Presentation to

The Twenty-Second Reaction Mechanisms Conference
at
Pittsburgh, Pennsylvania
University of Pittsburgh
14 June, 1988

University of Massachusetts
Department of Chemistry
Amherst, MA 01003

Submitted June 22, 1988

INTRODUCTION

Magnetic materials are of great importance in m technology, especially in computers. To date, pr applications of magnetism generally require use o ferromagnetic transition metals, especially iron. Qualitative theoretical predictions have indicated that certain ty organic materials will exhibit high-spin magnetic e (super-paramagnetism), and may in principle allow cre domains of purely organic ferromagnetism. Although the been isolated reports of organic polymeric ferro materials[1-2], much work is needed to clarify common st features and potential synthetic paths to putative ferromagnets. We are engaged in both theoreti experimental efforts to understand and create superparamagnetic[3] and ferro magnetic materials, using polyradical systems.

1. Yu. V. Korshak, T. V. Medvedeva, A. A. Ovchinnikov, V. N. Spektor Nature, 326, 370(1987).

2. J. B. Torrance, S. Oostra, A. Nazzad Synth. Metals, 19, 708(1987).

3. Cf., for instance, Y. Teki, T. Takui, K. Itoh, H. Iwamura, K. Kobayashi J. Am. Chem. Soc., 108, 2147(1986).

PROPOSED AND ONGOING INVESTIGATIONS

THEORETICAL WORK

Use molecular mechanics and semiempirical AM1 (AMPAC) to predict geometries of model polyradical systems.

Use AMPAC and INDO-CI to obtain related energies for states of different multiplicity -- is high spin preferred, and for what type of pi-system connectivities? how great is the gap from ground to excited state?

Use ab initio theory for select small diradicals that are potential models for monomeric units of polymers.

Theory can serve as the guide for experiment.

EXPERIMENTAL WORK

Develop a convenient method to generate polyradicals (esp. phenoxy) thermally and photochemically

Synthesize polyradical models to polymeric polyradical super-paramagnets

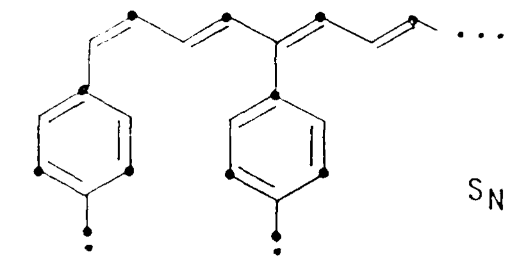
Study methods to generate and study polyradical models in matrix and in solid solution with an inert polymer

Eventually, use lessons learned from model studies to aim at synthesis of polymeric polyradical ferromagnets

Experiment is the crucial test of theory

BACKGROUND -- THEORETICAL STRUCTURAL REQUIREMENTS

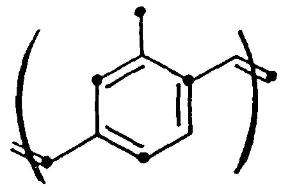
CONNECTIVITY in conjugated pi-radical polymers



alpha spin site

beta spin site

$S_N = (N_\bullet - N_\cdot)_n \; \text{--->} \; \infty$

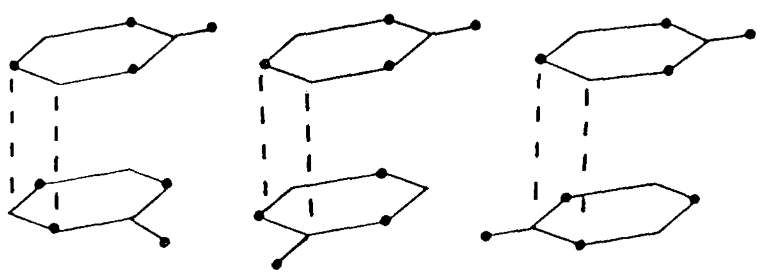


monomer $N_\bullet - N_\cdot = 1$

so $S_N \text{-->} \infty$

Thus, a polymer chain of *odd alternant radical units in* pi-conjugation is qualitatively predicted to be superparamagnetic (high-spin).

3-D STACKING in conjugated pi-radicals



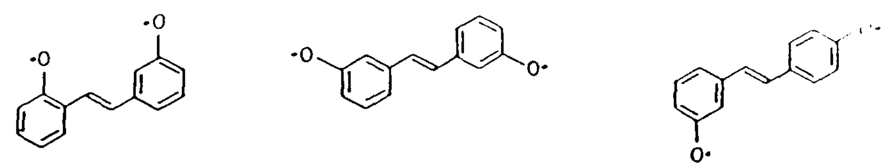
triplet singlet triplet PREDICTED

McConnell has predicted the qualitative effect of various geometries on coupling between alternant radicals, and which types of coupling should lead to high-spin (ferromagnetic) spin states. The important criterion is to allow coupling of sites with opposite (alpha vs. beta) spin-density.

THEORETICAL FINDINGS

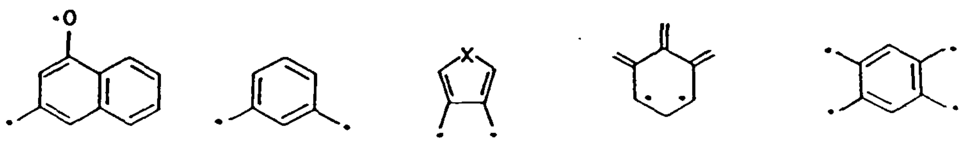
CONNECTIVITY EFFECTS ON POLYRADICAL GROUND STATES

Oligomeric models



INDO T-S gap kcal/mol	2.5	0.4	-2.0

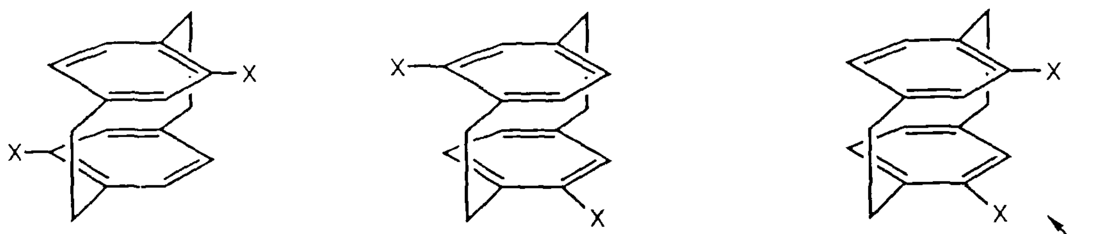
Monomeric models



INDO T-S gap	18.6	11.9	-0.6	4.0	-11.3
ab initio	-	10.1	-1.7	-	-6.6
expt.	T	T	S	In progress at UMass	In progress at Yale

These are examples among a large number of INDO-CI calculations supported by ab initio work and confirmed by experiment.
RESULT -- The INDO-CI model seems sufficient for semi-quantitative predictions of ground state multiplicity.

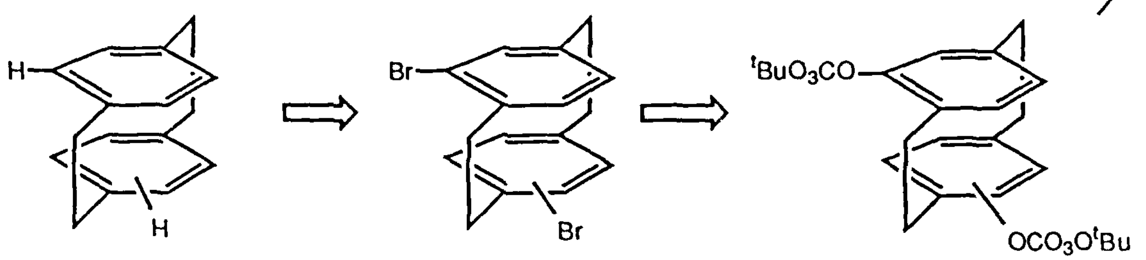
Computations qualitatively confirm the McConnell model for the dioxoy p-cyclophanes.



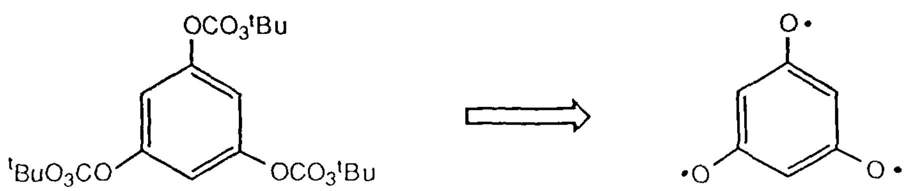
AM1-CISD T-S

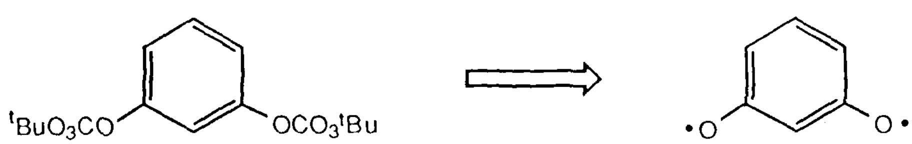
for X = O•	0.2 kcal/mol	0.1	0.5
for $X = CH_2\bullet$	0.1	0.0	0.3

Synthesis of these molecules is in progress.

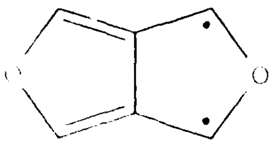


Synthesis of other potentially high-spin phenoxy-type radicals is also in progress.





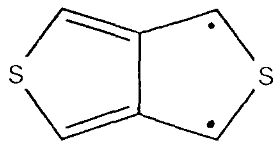
Use of semiempirical MNDO-UHF geometries and INDO-CISD spectral energies yields useful, interesting generalization of trends, even among dirdicaloid (rather than diradical) species.



15

^1A_g	0.0
$^3B_{2u}$	12.9

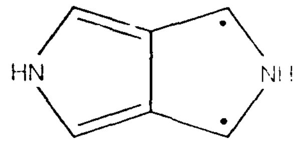
4n+2 species



16

^1A_g	0.0
$^3B_{2u}$	10.2

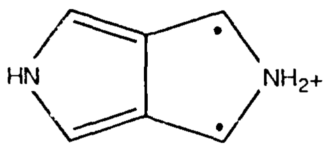
4n+2 species



17

^1A_g	0.0
$^3B_{2u}$	25.2

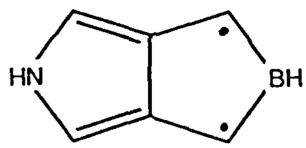
4n+2 species



19

$^1A_1$	0.0
$^3B_2$	5.1

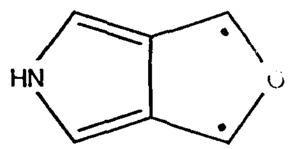
4n species



20

$^1A_1$	0.0
$^3B_2$	5.3

4n species



21

$^1A_1$	0.0
$^3B_2$	13.3

4n species
+2

DEVELOPMENT OF RADICAL GENERATION CHEMISTRY

STRATEGY:

It would be useful to produce phenoxy radicals thermally or photochemically. In principle, one might thereby produce a magnetic record in a polymer containing polyradical precursors by irradiation or heating. A fairly active moiety is needed to produce radicals, yet with sufficient stability to allow subsequent chemistry in preparing a polymer.

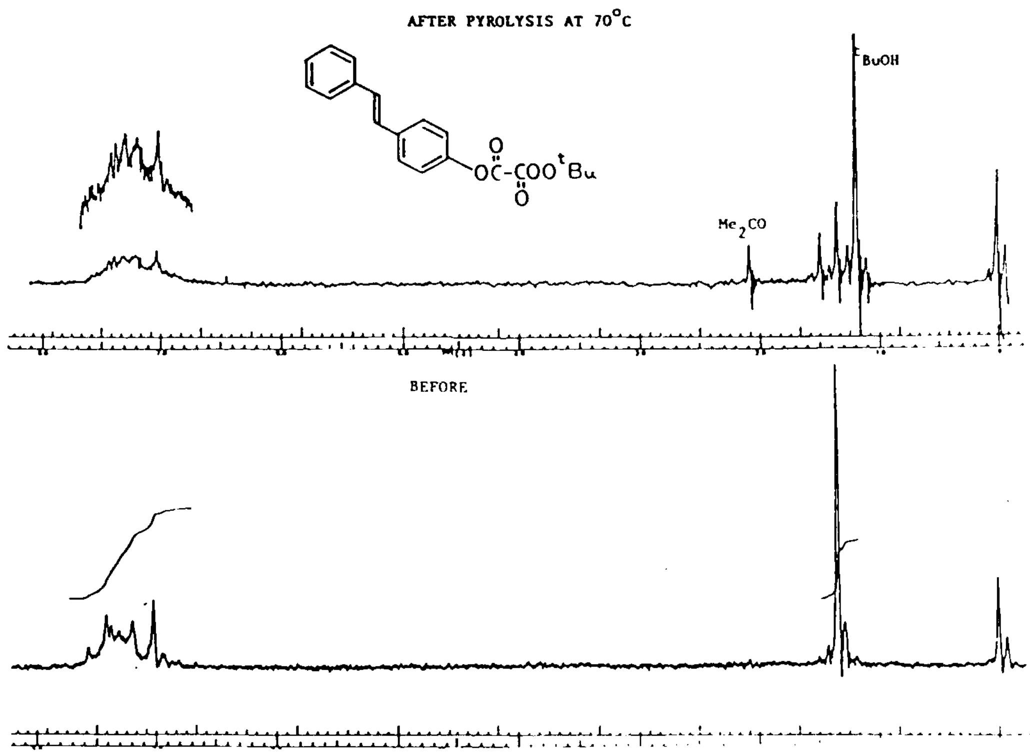
PRESENT SOLUTION:

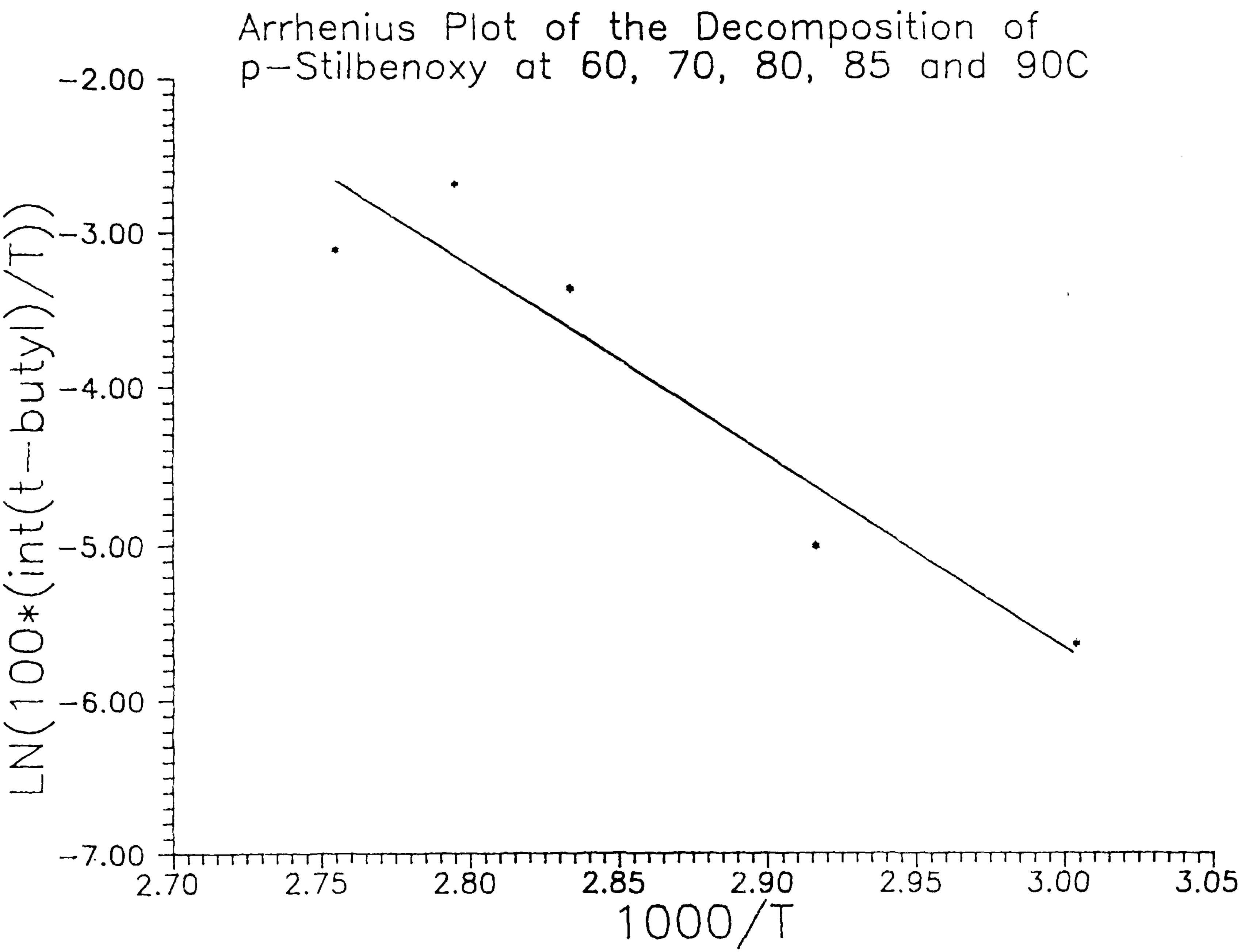
$$^{t}Bu\text{-}OOH \; + \; Cl\text{-}\overset{O}{C}\text{-}\overset{O}{C}\text{-}Cl \xrightarrow[CCl_4]{} {}^{t}Bu\text{-}OO\text{-}\overset{O}{C}\text{-}\overset{O}{C}\text{-}Cl \rightarrow$$

$$\xrightarrow[CCl_4]{ArOH} {}^{t}BuO\text{-}O\text{-}\overset{O}{C}\text{-}\overset{O}{C}\text{-}O\text{-}Ar \xrightarrow[60^{\circ}]{85\%} {}^{t}BuO\cdot \quad CO_2 \quad CO \quad ArO\cdot$$

RESULT:

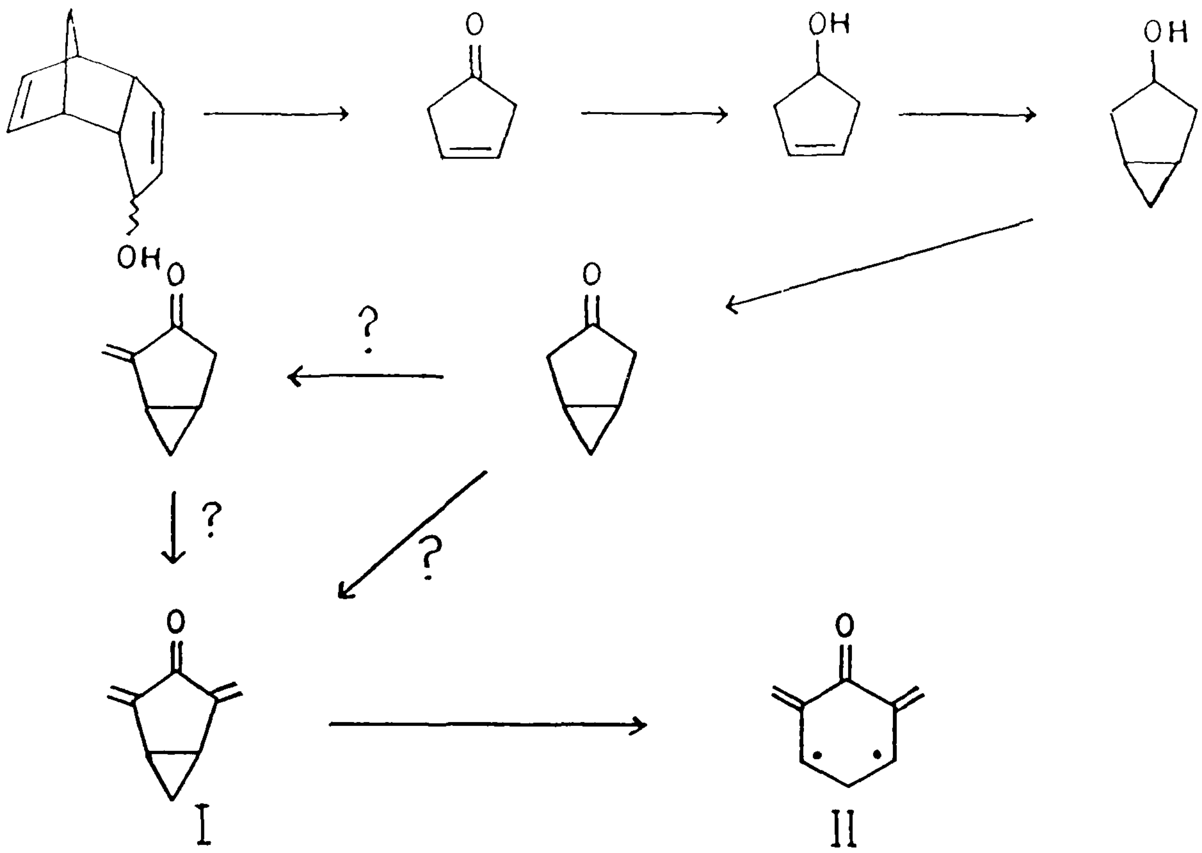
Decomposition of peroxyoxalates yield typical radical products.





Arrhenius Plot of the Decomposition of
p-Stilbenoxy at 60, 70, 80, 85 and 90C
LN(100*(int(t-butyl)/T))
1000/T
-2.00
-3.00
-4.00
-5.00
-6.00
-7.00
2.70
2.75
2.80
2.85
2.90
2.95
3.00
3.05

EXPERIMENTAL MODEL COMPOUNDS TESTS OF THEORY

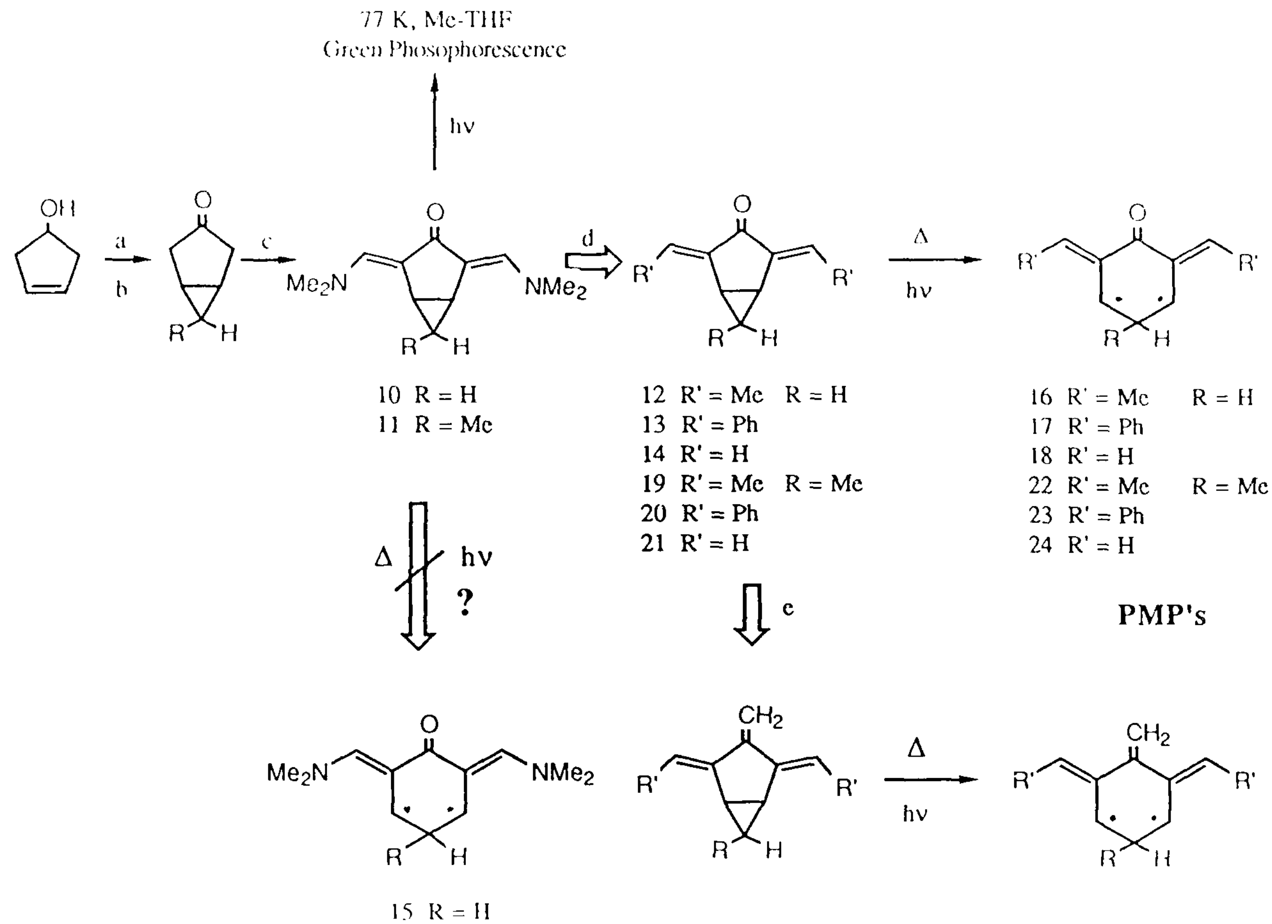


INDO/CI indicates small T-S gap for II (~1 kcal/mol)

GOALS:

1) Final bis-methylenation to give diradical precursor I. INDO-CI predicts triplet ground state, supported by ab initio theory
2) Low temperature matrix photolysis of I, looking for triplet EPR signal and UV-vis absorption attributable to II
3) Determine stability of triplet II, as a potential monomer in an organic magnetic material

PENTAMETHYLENEPROPANES ARE AN INTERESTING CLASS OF DIRADICALS WHICH WE ARE STUDYING THEORETICALLY AND EXPERIMENTALLY.



a - RCH_2I_2 / Zn-Cu ; b - PDC, CH_2Cl_2 ; c - $(^tBuO)_2CHNMe_2H^+ CF_3CO_2^-$, Δ ; d - R'Li, Et_2O ; e - Wittig, Petersen olefination

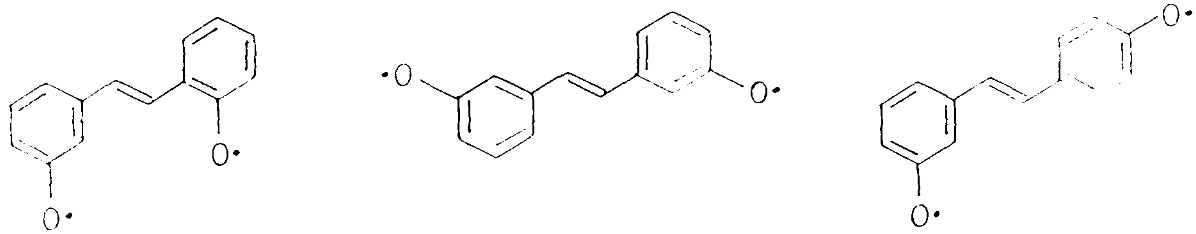
⇨ In progress

→ Completed

INDO-CISD indicates a modest (1-3 kcal/mol) favoring of the triplet state for PMP's, in agreement with ab initio computations by ourselves and others.

FUTURE PROSPECTS

SYNTHESIS OF POLYRADICAL MODELS



DEVELOPMENT OF OTHER RADICAL PRODUCING MOIETIES

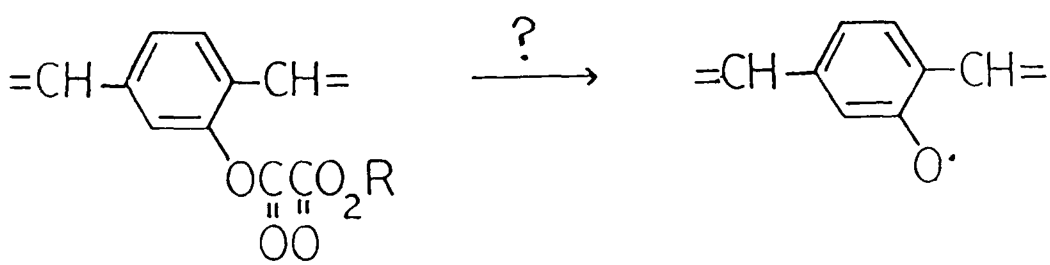
$$Ar{-}O{-}\overset{O}{\overset{\|}{C}}{-}O{-}O{-}C(R)_2{-}N{=}N{-}R'$$

$$\Downarrow$$

$$Ar{-}O^{\cdot} \quad + (CO_2 \quad R_2C{=}O \quad R'^{\cdot})$$

cf. J. Warkentin et al., J. Am. Chem. Soc., 103, 7189(1981).

BUILDING RADICALS INTO POLYRADICAL POLYMERS



TECHNICAL REPORT DISTRIBUTION LIST, GEN

	No. Copies
Office of Naval Research Attn: Code 1113 800 N. Quincy Street Arlington, Virginia 22217-5000	2
Dr. Bernard Douda Naval Weapons Support Center Code 50C Crane, Indiana 47522-5050	1
Naval Civil Engineering Laboratory Attn: Dr. R. W. Drisko, Code L52 Port Hueneme, California 93401	1
Defense Technical Information Center Building 5, Cameron Station Alexandria, Virginia 22314	12 high quality
DTNSRDC Attn: Dr. H. Singerman Applied Chemistry Division Annapolis, Maryland 21401	1
Dr. William Tolles Superintendent Chemistry Division, Code 6100 Naval Research Laboratory Washington, D.C. 20375-5000	1
Dr. David Young Code 334 NORDA NSTL, Mississippi 39529	1
Naval Weapons Center Attn: Dr. Ron Atkins Chemistry Division China Lake, California 93555	1
Scientific Advisor Commandant of the Marine Corps Code RD-1 Washington, D.C. 20380	1
U.S. Army Research Office Attn: CRD-AA-IP P.O. Box 12211 Research Triangle Park, NC 27709	1
Mr. John Boyle Materials Branch Naval Ship Engineering Center Philadelphia, Pennsylvania 19112	1
Naval Ocean Systems Center Attn: Dr. S. Yamamoto Marine Sciences Division San Diego, California 91232	1

DL/1113/87/2

ABSTRACTS DISTRIBUTION LIST, 356A

Professor C. H. Wang
Department of Chemistry
University of Utah
Salt Lake City, Utah 84112

Professor J. H. Magill
Department of Metallurgical
and Materials Engineerin
University of Pittsburg
Pittsburgh, Pennsylvania 15261

Professor R. Stein
Department of Polymer Science
and Engineering
University of Massachusetts
Amherst, Massachusettts 01002

Professor C.P.S. Sung
Institute of Materials Science
University of Connecticut
Storrs, Connecticut 06268

Professor M. Pomerantz
Department of Chemistry
University of Texas
Arlington, Texas 76019

Dr. L. Buckley
Naval Air Development
Code 6063
Warminster, Pennsylvania 18974

Dr. Thomas J. McCarthy
Polymer Science and
Engineering Department
University of Massachusetts
Amherst, MA 01003

Professor David S. Soong
Department of Chemical Engineering
University of California
Berkeley, CA 94720-9989

Professor Leo Mandelkern
Institute of Molecular Biophysics
Florida State University
Tallahassee, FL 32306-3015

Professor Scott E. Rickert
Department of Macromolecular Science
Case Western Reserve University
10900 Euclid Avenue
Cleveland, OH 44106

Professor Bruce Hudson
Department of Chemistry
University of Oregon
Eugene, OR 97403

Professor E. Samulski
Department of Chemical Engineering
University of Connecticut
Storrs, Connecticut 06268

Professor J. W. Doane
Liquid Crystal Institute
Kent State University
Kent, Ohio 44242

Professor A. Argon
Department of Mechanical
Engineering
Massachusetts Institute of
Technology
Cambridge, Massachusetts 02139

DR. PAUL LAHTI
UNIV OF MASSACHUSETTS
GRC-1602
AMHERST MA 01003
Columbus,

Dr. P. J. Hendra
Department of Chemistry
University of Southampton
Southampton S09 5NH
UNITED KINGDOM

Professor A. Heeger
Department of Physics
University of California
Santa Barbara, CA 93106

Professor Curtis W. Frank
Department of Chemical Engineering
Stanford University
Stanford, CA 94305

Professor John F. Rabolt
IBM K91 B801
Almaden Research Center
650 Harry Road
San Jose, CA 95120-6099

Dr. William B. Moniz
Chemistry Division
Naval Research Laboratory
Washington, D.C. 20375-5000

DL/1113/87/2

ABSTRACTS DISTRIBUTION LIST, 356A

Naval Surface Weapons Center
Attn: Dr. J. M. Augl, Dr. B. Hartman
White Oak
Silver Spring, Maryland 20910

Dr. Robert E. Cohen
Chemical Engineering Department
Massachusetts Institute of Technology
Cambridge, Massachusetts 02139

Dr. T. J. Reinhart, Jr., Chief
Nonmetallic Materials Division
Department of the Air Force
Air Force Materials Laboratory (AFSC)
Wright-Patterson AFB, Ohio 45433

Professor J. Lando
Department of Macromolecular Science
Case Western Reserve University
Cleveland, Ohio 44106

Professor J. Scheinbeim
Department of Materials Science
and Mechanics
Rutgers University
Piscataway, New Jersey 08854

PLASTEC
DRSMC-SCM-O(D), Bldg 351 N
Armament Research & Development
Center
Dover, New Jersey 07801

Dr. Ivan Caplan
DTNSRDC
Code 0125
Annapolis, MD 21401

Professor H. Ishida
Department of Macromolecular Science
Case Western Reserve University
Cleveland, OH 44106

Professor F. Rodriguez
Department of Chemical Engineering
Cornell University
123 Day Hall
Ithaca, New York 14853

Dr. W. R. Krigbaum
Department of Chemistry
Duke University
Durham, North Carolina 27706

Professor J. T. Koberstein
Department of Chemical Engineering
University of Connecticut
Storrs, Connecticut 06268

Professor J. K. Gillham
Department of Chemical and Engineering
Princeton University
Princeton, New Jersey 08540

Professor L. H. Sperling
Department of Chemical Engineering
Lehigh University
Bethlehem, Pennsylvania 18015

Professor Brian Newman
Department of Mechanics and
Materials Science
Rutgers University
Piscataway, New Jersey 08854

Dr. C. E. Hoyle
Department of Polymer Science
University of Southern Mississippi
Hattiesburg, Mississippi 39406

Dr. Stuart L. Cooper
Department of Chemical Engineering
University of Wisconsin
Madison, Wisconsin 53706

Professor Sukant K. Tripathy
Department of Chemistry
University of Lowell
Lowell, Massachusetts 01854

Dr. B. Gordon III
Department of Materials Science
Pennsylvania State University
University Park, PA 16802

Dr. I. M. Brown
McDonnell Douglas Research Laboratories
P.O. Box 516
St. Louis, Missouri 63166

Dr. L. E. Sloter
Code Air 931-A
Naval Air Systems Command
Washington, D.C. 20361-9310