Non-Kekulé Molecules - Theory, Practice and Uses

INDO-CI and AMI-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 superparamagnetic species. Peroxyxalate esters are useful photo and thermal precursors which are fairly stable at room temperature, but photo-chemically and thermally (>70°C) labile.
NON-KEKULE MOLECULES -- THEORY, PRACTICE, AND USES

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INTRODUCTION

Magnetic materials are of great importance in magnet technology, especially in computers. To date, practical applications of magnetism generally require use of strong ferromagnetic transition metals, especially iron. Qualitative theoretical predictions have indicated that certain types of organic materials will exhibit high-spin magnetic effects (super-paramagnetism), and may in principle allow creation of domains of purely organic ferromagnetism. Although there have been isolated reports of organic polymeric ferromagnets, materials\(^1\)\(^-\)\(^2\), much work is needed to clarify common structural features and potential synthetic paths to putative organic ferromagnets. We are engaged in both theoretical and experimental efforts to understand and create superparamagnetic\(^3\) and ferromagnetic materials, using polyradical systems.


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 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

\[ S_N = (N_\alpha - N_\beta)_n \rightarrow \infty \]

monomer \( N_\alpha - N_\beta = 1 \)
so \( S_N \rightarrow \infty \)

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

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  T  T  S  In progress  In progress
expt.  -  10.1  -1.7  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.

\[
\text{AM1-CISD TS}
\]

for \( X = \text{O} \cdot \) \( 0.2 \text{ kcal/mol} \) 0.1 0.5

for \( X = \text{Cl}_2 \cdot \) 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 diradicaloid (rather than diradical) species.
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:

\[
\text{tBu-OOH} + \text{Cl-C-C-Cl} \xrightarrow{\text{cc1}_4} \text{tBu-OO-C-C-Cl} \rightarrow \\
\text{ArOH} \xrightarrow{\text{cc1}_4} \text{tBuO-O-C-C-O-Ar} \xrightarrow{85\%} \text{BuO}^- \cdot \text{CO}_2 \cdot \text{CO} \cdot \text{ArO}^-
\]

RESULT:

Decomposition of peroxyoxalates yield typical radical products.

AFTER PYROLYSIS AT 70°C

BEFORE
Arrhenius Plot of the Decomposition of p-Stilbenoxyl at 60, 70, 80, 85 and 90°C
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.

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

\[
\begin{align*}
\text{Ar-O-C-O-O-C(R)₂-N=N-R'} & \\
\downarrow & \\
\text{Ar-O·} + (\text{CO}_2 \ R_2\text{C=O} \ R'·) & \text{cf. J. Warkentin et al., J. Am. Chem. Soc., 103, 7189 (1981).}
\end{align*}
\]

BUILDING RADICALS INTO POLYRADICAL POLYMERS

\[
\text{=CH-CH=} \quad ? \quad \text{=CH-CH=}
\]
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