OFFICE OF NAVAL RESEARCH

END-OF-THE-YEAR REPORT

PUBLICATIONS/PATENTS/PRESENTATIONS/HONORS/STUDENTS REPORT

for

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R&T Code 4135010

"Design of Organic Nonlinear Optical Materials"

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Part I

a. Papers Submitted to Refereed Journals (and not yet published)


b. Papers Published in Refereed Journals


c. Books (and sections thereof) Submitted for Publication


d. Books (and sections thereof) Published

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e. Technical Reports Published and Papers Published in Non-Refereed Journals

f. Patents Filed

"Optically Nonlinear Aromatic Carboxylic Acid Complexes," Pat. applied for October, 1988

g. Patents Granted

h. Invited Presentation at Topical or Scientific/Technical Society Conferences

1990

Southern Illinois University
University of Minnesota, Duluth
Hunter College, New York
Biosym Technologies, San Diego, California
Polaroid Corporation, Cambridge
Ohio State University
University of Missouri - St. Louis
Purdue University, Chemistry Department
Purdue University, School of Pharmacy
Uppsala University, Sweden
University of Stockholm, Sweden
University of Copenhagen, Denmark
Cambridge, England
3M Company
Upjohn Company
Aerojet Corporation
Southern Illinois University
Monsanto Company

Symposium on Nonlinear Optical Materials, ACS Meeting, Boston
Proteins and Peptides, Gordon Conference, Ventura California
3rd Annual Midwest Organic Solid-State Chemistry Meeting, Purdue
International Union of Crystallography, Bordeaux, France
Conference on Molecular Recognition, Berlin
2nd National Symposium on Frontiers of Science, Irvine, California

i. Contributed Presentations at Topical or Scientific/Technical Society Conferences

1990

ACA Meeting: April 1990
"Using Hydrogen Bonding to Change the Solid State Environment of p-Nitroaniline, (Susan Reutzel)
"The Use of Hydrogen Bonds in the Preparation of Imide Cocrystals" (Kin-Shan Hauung)
Linus Pauling Award for poster presentation (Susan Reutzel)
Midwest Organic Solid State Chemistry Symposium: June, 1990
"Applications of Solid-State NMR to the Design of Imide Cocrystals" (Susan Reutzel)
"Hydrogen-bond Selectivity During Formation of Pyridine/Benzoic Acid Cocrystals: Solid-State IR as a Diagnostic Tool" (John MacDonald)
"Using Hydrogen Bonding to Change the Solid-State Environment of P-Nitroaniline" (Kin-Shan Huang)

Minnesota Science Academy Annual Meeting: May, 1990
"Molecular Recognition and Hydrogen Bond Properties of Diarylureas in the Solid-State" (Mohammad Zia-Ebrahimi)
Newton W. Winchell Award for Undergraduate Research (Mohammad Zia-Ebrahimi)

University of Minnesota, May 1990
Presidential Student Leadership Award for activities as the President of the American Chemical Society Student Affiliates Chapter (Mohammad Zia-Ebrahimi)

j. Honors/Awards/Prizes

M.C. Etter, Iota Sigma Pi Award, Minnesota Chapter, for Excellence in Chemistry

k. Number of Graduate Students Receiving Full or Partial Support on ONR Contract

Total: 4    Minorities: 2    Asian*: 1

l. Number of Postdoctoral Fellows Receiving Full or Partial Support on ONR Contract

0

m. Other funding

Agency: United States/Israel Binational Science Foundation Grant
Grant title: "Environmental Influences on Molecular Conformation and Physical Properties of Drugs"
Amount: $30,000    Period of Performance: 1987-1990

Agency: Petroleum Research Fund - AC
Grant title: "Solid-state NMR Studies of Hydrogen-Bonded Materials"

Agency: Sloan Foundation
Grant title: "Organic Solid- State Chemistry"

Agency: National Institutes of Health
Grant title: "Hydrogen Bond Rules for Organic Compounds"

Agency: National Science Foundation
Grant title: "Hydrogen-Bonded Supermolecules: A New Approach to the Synthesis of Host-Guest Complexes Chemistry"
Amount: $204,100    Period of Performance: 1989-1990
Part II

a. Margaret C. Etter

b. Hal Guard

c. (612) 624-5217

d. Brief description of project

This project deals with a new approach to designing organic nonlinear optical materials for second harmonic generation based on the use of hydrogen bonding to organize molecules into acentric arrays. Since crystal engineering is not a well developed science we cannot yet predict crystal packing patterns for even simple organic molecules. For organic nonlinear optical materials this dilemma means that even the most promising organic molecule may have poor to nonexistent nonlinear optical properties because it forms centric crystals or crystals with unfavorable molecular dipole alignments. Our work is aimed at gaining control over the crystal growth process by understanding the molecular basis for aggregation and nucleation. Using hydrogen bonds as one of the strongest, most prevalent, and most easily identified intermolecular interactions, we have found that we can predict the primary structure of hydrogen-bonded aggregates based on functional group complementarity and stereoelectronic considerations. We use this information to choose (or synthesize) molecules with hydrogen-bonding groups positioned on the molecules so that acentric hydrogen-bonded aggregates must necessarily form. We prepare crystals of these compounds, measure their second harmonic intensities, and solve their crystal structures.

e. Significant results during last year

1) Nitroaniline Cocrystals. Technical Report #5. This work demonstrates that nitroanilines can be crystallized with many different packing patterns by cocrystallizing them with a variety of proton-donor and acceptor guest molecules. The flexibility of this method and the possibility of predicting cocrystal formation and cocrystal packing patterns are discussed.

2) Dinitrourea Polymorphs. Technical Report #6. We found that the two metastable polymorphs of a dinitrourea compound are acentric and have moderate SHG. The crystal structure of one of these polymorphs has been done. It's structure is analyzed to determine why this polymorph is acentric why the most stable polymorph is not.

3) Symmetry Bias in Hydrogen-Bonded Crystals. Technical Report #7. We have found that compounds whose crystal structures contain acentric hydrogen-bonded networks are significantly more likely to have acentric space groups than structures with no hydrogen bonds or with centric hydrogen-bond patterns. This analysis was based on data extracted from the Cambridge Crystallographic Data Base for primary, secondary, and tertiary nitroanilines.

f. Brief summary of plans for next year's work

a) Solution Aggregation Studies. This work is aimed at detecting hydrogen-bonded aggregates in solution and demonstrating whether they have the same structure as the hydrogen-bonded aggregates in crystals that grow from these solutions. The idea is that we may be able to use solution methods to control and characterize the species that eventually control the structure of crystal nucleation sites. We are using vapor phase osmometry, variable temperature solution IR and NMR, and UV/VIS methods to characterize solutions and measure $K_{assoc}$ constants.
b) **Acentric and Chiral Nitroaniline Cocrystals and Cocrystal Analogs.** Now that we have mapped out the chemical principles for predicting when nitroaniline cocrystals will form, we can use our ideas about symmetry bias (Technical Reports #7) to design acentric nitroaniline cocrystals. We can also use this idea to prepare nitroaniline cocrystal analogs which are heterodimeric hydrogen-bonded pairs that have pendant nitro groups and aniline groups.

c) **Solid-State Cocrystallization Mechanisms.** We have found that most of the cocrystals that we have made by solution recrystallization methods can also be prepared by grinding the solid-state components together. To understand the mechanism of such an unusual yet nearly ubiquitous process, we are preparing phase diagrams to identify the stable phases of these complexes. X-ray powder patterns and chemical analyses will be done on the different phases, and phase transformations will be monitored by DSC to understand how bulk changes in the phase composition correlate with extent of formation of particular hydrogen-bonded species.

g. **List of names of graduate students and post-doctorals currently working on project.**
   Andrea Cicero
   Kin-Shan Huang
   John C. MacDonald
   Randy Wanke

h. **Technical Reports Submitted to ONR during the past year.**
4) "Controlling Symmetry and Asymmetry in Hydrogen-Bonded Nitroaniline Materials"
5) Nitroaniline Cocrystals
6) "Dinitrourea Polymorphs with SHG Properties"
7) "Symmetry Bias in H-Bonded Crystals"

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Part III

a-c. Attached

d. Cocrystallization can be used to expand the number of possible solid-state packing patterns available to a molecule. This method can be used to circumvent unfavorable packing symmetries, hydrogen-bond patterns, or charge-transfer interactions that might occur in the stable crystal forms of the molecule of interest. When a molecule has particularly favorable microscopic properties, such as hyperpolarizability, but unfavorable macroscopic properties, such as a zero $X(2)$, cocrystallization provides a mechanism for altering the macroscopic properties. In this report, the cocrystallization potential for p-nitroaniline is explored. Ten cocrystals of p-nitroaniline were prepared based on the principle that a guest molecule with a better proton-donating group than the aniline of PNA, or a better acceptor group than the nitro group, would compete with the self-association of PNA and give hydrogen-bond complexes. These complexes then nucleate the crystallization of cocrystals. Three cocrystals were also prepared of m- and o-nitroaniline to demonstrate the versatility of this method. The next step is to choose guest acceptors that will cocrystallize with PNA and form acentric hydrogen-bonded networks as a way to bias the final crystal structures to be acentric.
MULTIPLEXING ORGANIC COMPOUNDS:
The Case of PNA

Margaret C. Etter
University of Minnesota

The Problem:

PNA (p-nitroaniline) crystallizes in a centric space group, so it cannot exhibit second order nonlinear optical effects.

PNA stubbornly refuses to crystallize in other polymorphs.

The Goals:

To grow multiple crystal forms of organic compounds by controlling their intermolecular chemistry.

Ultimately, to design acentric PNA solid-state materials.

The Methods:

To form cocrystals of PNA with organic guest molecules of varying size and symmetry.

Initially, to test the versatility of PNA as a cocrystallization host.

To use acentric hydrogen-bond interactions to control the symmetry of the crystalline environment of PNA.
PNA cocrystallizes with the following guest molecules:

The following three hydrogen-bond types are observed:
**Results:**

PNA will cocrystallize with a variety of guest donor and acceptor molecules.

The driving force for cocrystallization is formation of strong intermolecular host/guest hydrogen bonds.

*m* - and *o*-Nitroanilines also cocrystallize easily.

**The Next Steps:**

To choose guest molecules that will induce acentricity in the final host/guest crystals.

There are two types of guest molecules that are potential candidates:
- chiral guests like unsymmetrical phosphine oxides
- guests that form acentric hydrogen-bond patterns, like disubstituted ureas

Testing SHG of PNA cocrystals on our Kurtz/Dougherty powder SHG device.