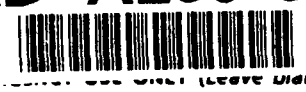
MASTER COPY KEEP THIS COPY FOR REPRODUCTION PURPOSES

2

# AD-A260 996



## ENTATION PAGE

Form Approved
OMB No. 0704-0188



| 2. REPORT DATE | 3. REPORT TYPE AND DATES COVERED |
|---|---|
| DEC 21, 1992 | Final 1 Sep 89 - 30 Nov 92 |

**4. TITLE AND SUBTITLE**
MOLECULAR DEVICES BASED ON NEW MONOLAYER-FORMING SYSTEMS

**5. FUNDING NUMBERS**
DAAL03-89-G-0094

**6. AUTHOR(S)**
CRAIG J. ECKHARDT



**7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)**
UNIVERSITY OF NEBRASKA-LINCOLN
524 HaH
Lincoln, NE 68588-0304

**8. PERFORMING ORGANIZATION REPORT NUMBER**

**9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)**
U. S. Army Research Office
P. O. Box 12211
Research Triangle Park, NC 27709-2211

**10. SPONSORING/MONITORING AGENCY REPORT NUMBER**
ARO 27195.1-CH-SP

**11. SUPPLEMENTARY NOTES**
The view, opinions and/or findings contained in this report are those of the author(s) and should not be construed as an official Department of the Army position, policy, or decision, unless so designated by other documentation.

**12a. DISTRIBUTION/AVAILABILITY STATEMENT**
Approved for public release; distribution unlimited.

**12b. DISTRIBUTION CODE**

**13. ABSTRACT** *(Maximum 200 words)*

The formation of novel planar lattices formed by monolayers of new amphiphilic molecules is reported. The rigid amphiphiles have cross-sections designed to provide two-dimensional crystals of the hexagonal, rectangular and oblique crystal classes. The packings are studied by atomic force microscopy. One amphiphile of triangular cross-section forms a hexagonal lattice. Two other amphiphiles, a tetracyclic and binapthyl, are chiral and synthesized as racemates. The single binapthyl amphiphile forms two commensurate lattices, rectangular and oblique, in the same monolayer. The tetracyclic amphiphile shows three phases on water and upon transfer at their respective formation pressures onto mica, three phases are observed: glass-like, rectangular and oblique. The oblique phase results as a phase separation of the enantiomers as a result of spontaneous resolution in two dimensions. Atom-atom potential calculation are shown to be essential to the design and understanding of these planar lattices. The results have important implications beyond monolayer chemistry and physics for fields such as liquid crystals and biophysics.

| 14. SUBJECT TERMS | 15. NUMBER OF PAGES |
|---|---|
| Monolayer films; Langmuir-Blodgett films, spontaneous optical resolution, commensurate lattices, phase transitions; packing | 5 |
| | 16. PRICE CODE |

| 17. SECURITY CLASSIFICATION OF REPORT | 18. SECURITY CLASSIFICATION OF THIS PAGE | 19. SECURITY CLASSIFICATION OF ABSTRACT | 20. LIMITATION OF ABSTRACT |
|---|---|---|---|
| UNCLASSIFIED | UNCLASSIFIED | UNCLASSIFIED | UL |

# MOLECULAR DEVICES BASED ON NEW MONOLAYER-FORMING SYSTEMS

Final Report

Prepared by: Craig J. Eckhardt

December 22, 1992

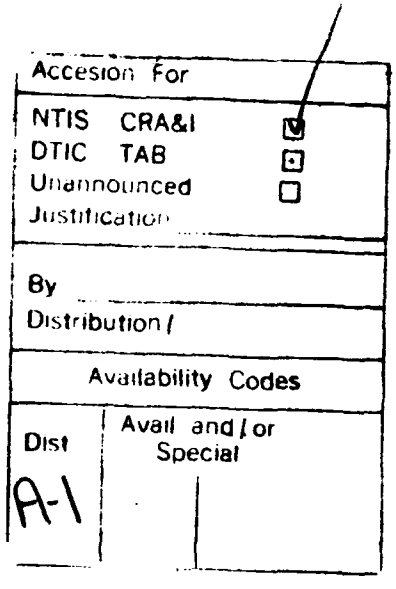
U. S. Army Research Office

Grant No.: DAAL03-89-G-0094

University of Nebraska-Lincoln

Approved for Public Release

Distribution Unlimited



## A. Statement of Problem Studied

The object of this research was to devise amphiphilic molecules that would pack into arrangements that had not been previously observed and that would lead through subsequent modification to the formation of smart materials. By establishing the ability to create desired planar lattices, especially acentric ones, through design of the amphiphiles comprising them, it then is possible to create smart monolayer materials. A major aspect of the work is the formulation of syntheses of rigid molecules possessing cross-sections that will yield the desired packing. Introducing chirality into these molecules is another aspect of the research problem. Subsequent to synthesizing the new amphiphiles, the major objectives were the task of forming monolayer films, their deposition on substrates, and their structural characterization through calculation and measurement.

## B. Summary of Most Important Results

The project has been successful in the design and synthesis of two new amphiphiles. One is a fused tetracyclic alcohol (TCA) and the other is an alkyl-substituted binapthyl alcohol (BHBN): The third amphiphile (TNB), a carboxylic acid, was a modification of a trinorborane molecule that had been synthesized in the laboratory of Peter Beak of the University of Illinois-Urbana: The first two are chiral and are produced as racemates. The last amphiphile is not chiral. All three are found to form monolayers on aqueous sub-phase.

While hexagonal packing has been reported for fatty acid amphiphiles, this packing is believed to be more a result of thermal and disordered positional averaging rather than a true hexagonal packing. The TNB deposited as a monolayer on mica is shown by atomic force microscopy (AFM) imaging to form, within error of the measurement, a hexagonal lattice. To obtain the most closely packed geometry, *i.e.* smallest effective area per molecule, it has proven necessary to repeatedly expand and compress the film. This arises because the monolayer

crystal must be annealed so that the TNB molecules will mesh into their "lock-and-key" structure. The unique "lock-and-key" structure of this film obviates the possibility that the hexagonal structure results from disorder or thermal averaging. In fact, it results from exploitation of the cross-sectional geometry of the TNB molecule which itself globally has the shape of a hexagonal unit cell. Local sections of the molecule are more triangular. Nevertheless, the TNB molecule cross-sectional geometry clearly dictates the packing in the planar lattice. This confirms the hypothesis that specific structures of planar lattices can be dictated by deliberate design of molecular geometry.

The BHBN molecule forms monolayers of quite extensive coherence. Formation on the aqueous subphase is normal and the collapse pressure is similar to that of fatty acid films. Langmuir-Blodgett transfer was made onto mica plates. Orientational coherence at least on the order of a square micron were observed by AFM. Translational coherence appears to also be on this scale but cannot be demonstrated conclusively without more detailed diffraction studies. The monolayer formed by the BHBN amphiphile is particularly unusual in that it comprises *two* separate nets. In essence, a single BHBN amphiphile forms two separate but *commensurate* planar lattices. The chiral binaphthyl section of the BHBN must pack in a centered rectangular space group as required of a racemic mixture. However, the hexyl chains are observed to form an oblique (distorted hexagonal) lattice. Because of chemical bonding, the two lattices are formed by the same molecule and are constrained to effect packings which will stay in registry. This provides an entirely new way of viewing packing in two dimensional systems and for the design of multilayer systems.

The TCA molecule displays an unusual surface isotherm. Three phases are indicated to be formed on water. Langmuir-Blodgett transfer of a monolayer on mica was effected for each of the three observed phases. AFM images obtained for each phase differed. The lowest pressure phase image was essentially that of a two-dimensional glass. The intermediate pressure phase was that of a centered rectangular lattice. This phase exhibits large orientational coherence and is completely consistent with a planar lattice that is formed by a racemate. The

image of the high temperature phase is remarkable in that it displays phase separation of regions formed by either of two oblique planar lattices which are mirror images of each other. This provides direct evidence that the TCA is undergoing spontaneous optical resolution in two dimensions and, as such, is its first observation in two-dimensional systems.

Theoretical treatment of these systems has been an important aspect of the research. In particular, atom-atom potential results have proven imperative for the understanding of the packing in BHBN. Further, the calculations have shown that the spontaneous resolution of TCA is consistent with the lattice energetics of the oblique and rectangular phases. The calculations are now well enough developed that they have great predictive value for design of amphiphiles for formation of planar lattices.

These results have impact far beyond monolayer physics and chemistry. It is of particular relevance to other disciplines in which chiral interactions between molecules are significant, such as liquid crystals and biophysics.

**C. List of All Publications**

"Crystal Engineering in Two Dimensions: A Calculative Investigation", *Chem. Phys. Lett.*, C. J. Eckhardt and D. R. Swanson.

"Crystal Engineering in Two Dimensions: Design of Amphiphiles for Coherent Films," *Langmuir*, N. M. Peachey, D. R. Swanson, C. J. Eckhardt, J.-H. Kim, R. A. Uphaus, G. P. Lutz and P. Beak.

"Crystal Engineering in Two Dimensions: Application of Close Packing Principle to an LB Film", *Langmuir*, D. R. Swanson and C. J. Eckhardt.

"Crystal Engineering in Two Dimensions: Design of Amphiphiles using the Close-Packing Principle," *Acta Chim. Hungar.*, Kitaigorodsikii Memorial Issue, (invited paper), in press, C. J. Eckhardt.

"Spontaneous Separation of Pure Enantiomers in Racemic Monolayer Crystals," *Nature*, (under revision pending publication, 1992) C. J. Eckhardt, N. M. Peachey, D. R. Swanson, J. M. Takacs, M. A. Khan, X. Gong, J.-H. Kim, J. Wang, and R. A. Uphaus.

**D. List of All Participating Scientific Personnel**

Faculty:

P. H. Dussault
C. J. Eckhardt
J. M. Takacs
R. A. Uphaus

Postdoctoral:

X. Gong
M. Pelter
S. Pyun
J. Zhu

Graduate Students:

J.-H. Kim, Ph.D., 1992, Iowa State University
N. M. Peachey
D. R. Swanson
C. Uche
D. Wang, M. S., 1992
J. Wang

**E. Report of Inventions:** None reported.