UCLA

Amphidynamic Materials-I

Miguel A. Garcia-Garibay
University of California, Los Angeles

José Nuñez
Peter Jarowski
Steve Karlen
Carlos Godinez
T-Alfredo V. Khuong
Marino Resendiz
Zach O'Brien

Dr. Chris Mortko
Dr. Horacio Reyes
Dr. Stephanie Gould
Dr. Hung Dang
Dr. Marcia Levitus
Dr. Zaira Dominguez
Dr. Carlos Sanrame

UCLA
Dr. Jane Strouse
Dr. Saeed Khan
Dr. Robert Taylor
Prof. K. N. Houk
Prof. F. Hawthorne
Prof. Ben Schwartz

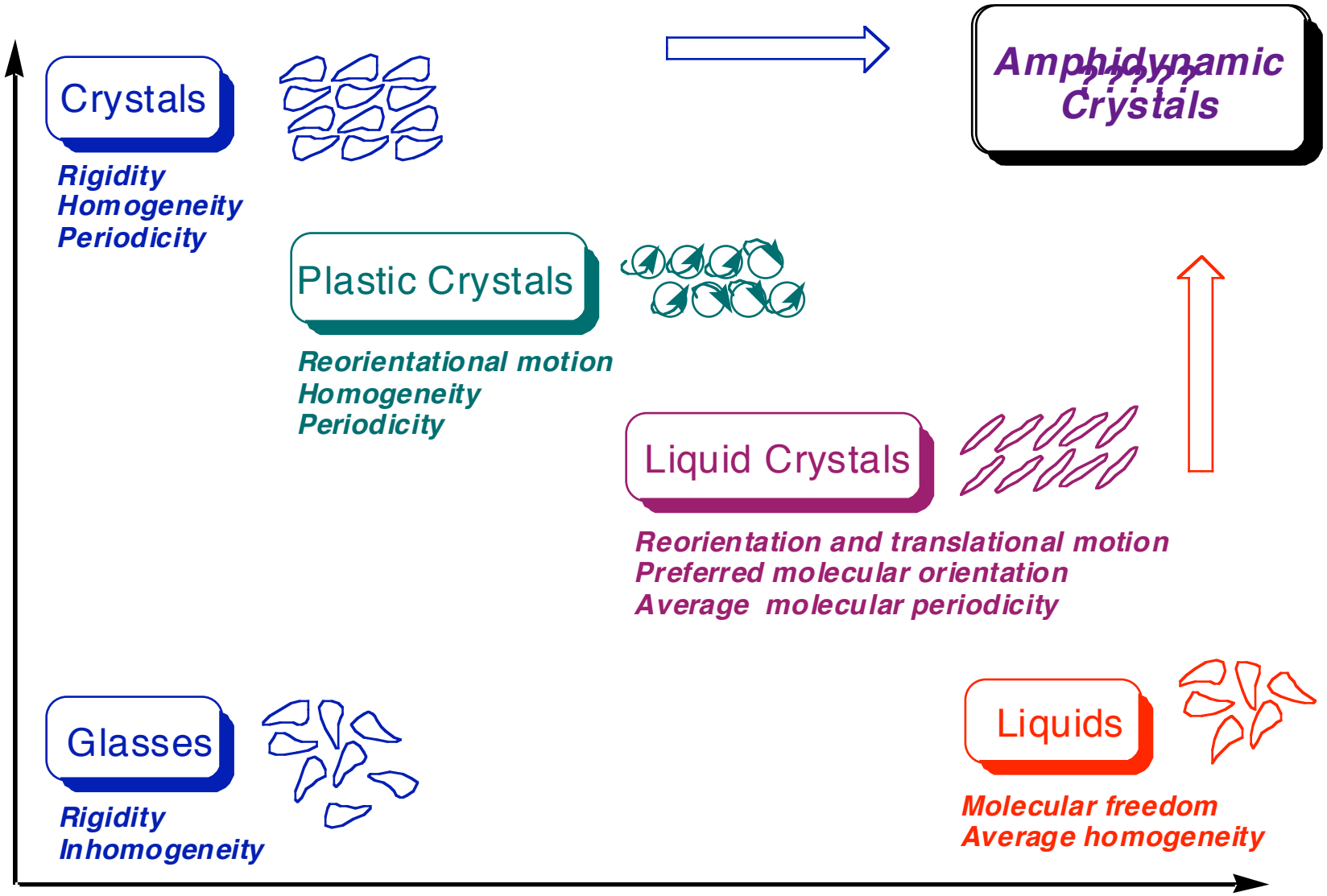
UC Boulder
Prof. John Price
Rob Horanski
Dr. Laura Clarke

Mexico
ENCB
Prof. Gerardo Zepeda

CINEVSTAV-IPN
Prof. Norberto Farfan
Pprof. Rosa Santillan

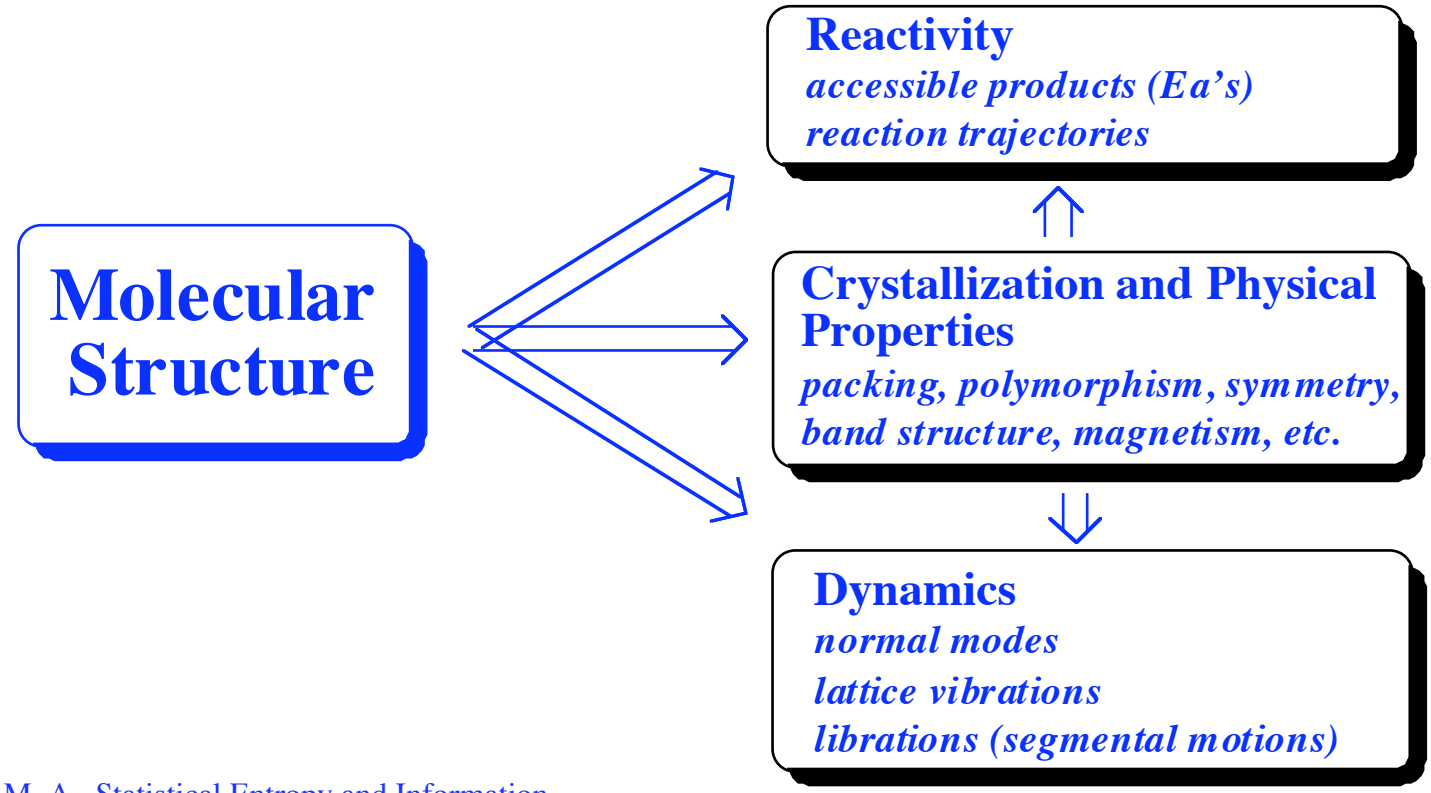
National Science Foundation

Condensed Phase Matter and Molecular Dynamics



Organic Solid State Chemistry

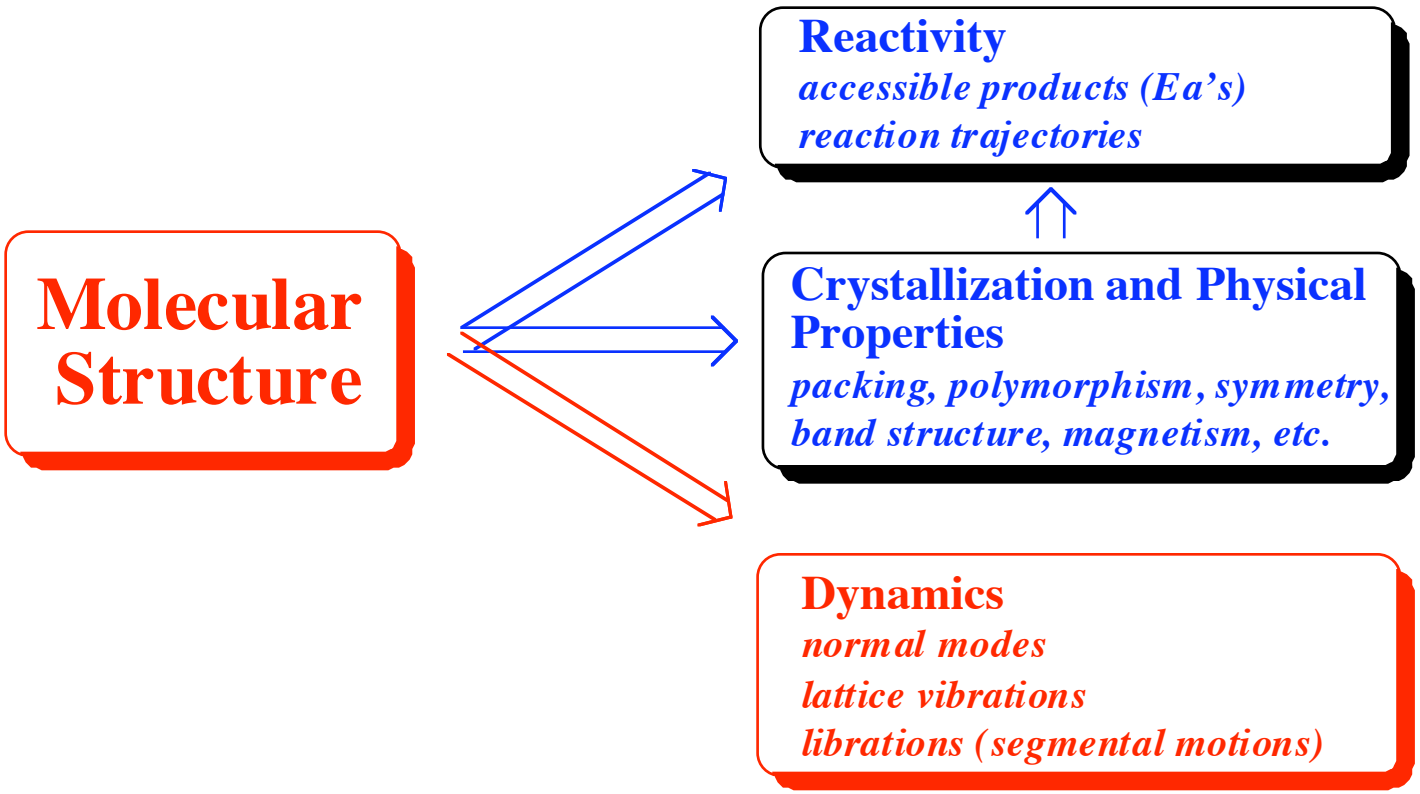
Solid State Properties



Garcia-Garibay, M. A., Statistical Entropy and Information in Crystals and Enzymes, *Curr. Opinion in Solid State and Material Science* **1998**, *3/4*, 399-406.

Organic Solid State Chemistry

Solid State Properties



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Amphidynamic Crystals:

Materials with functions and properties that rely on the structurally-programmed, collective and individual MECHANICAL motions of their constituent molecules

A Macroscopic Analog….

Replica of daVinci's adding machine

What is a machine? (Webster) a collection of parts that transmits forces motion and energy in a (structurally) pre-determined manner

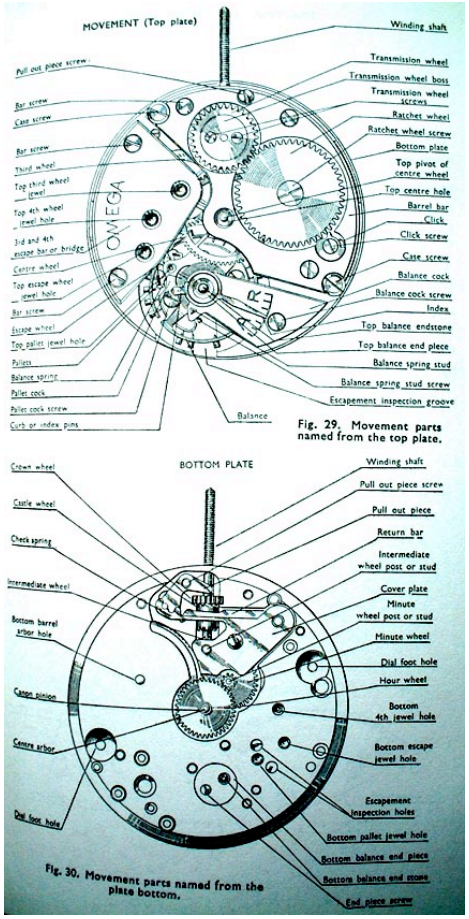
Can we formulate the definition of machine from a structure-dynamics perspective…

Blueprints = Structure and Dynamics Information

N-components
6N degrees of freedom

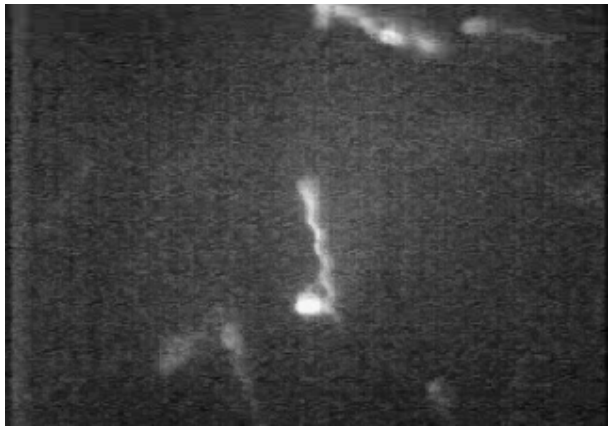
"Informed" Assembly →

1 Machine
6+1 degrees of freedom



In Molecules:
Structure <=> Energy
All Information

Bacterial Flagellum

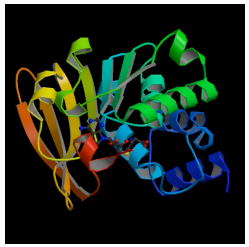


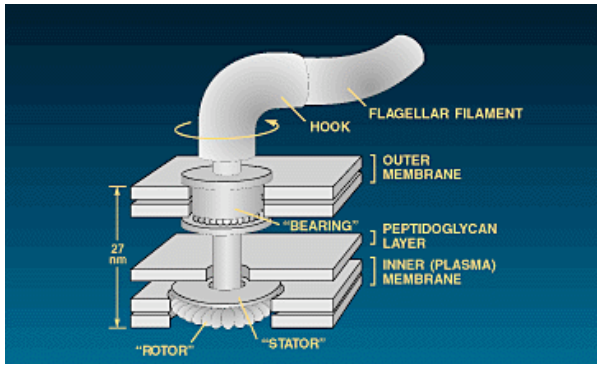
Biomolecular Machines

(supramolecular self-assembled systems, supported, input-output, stochastic…)

C H N O S

Amino acids





Structural hierarchies….

atomic —> molecular —> supramolecular

(Many levels of supramolecular structure can be noted)

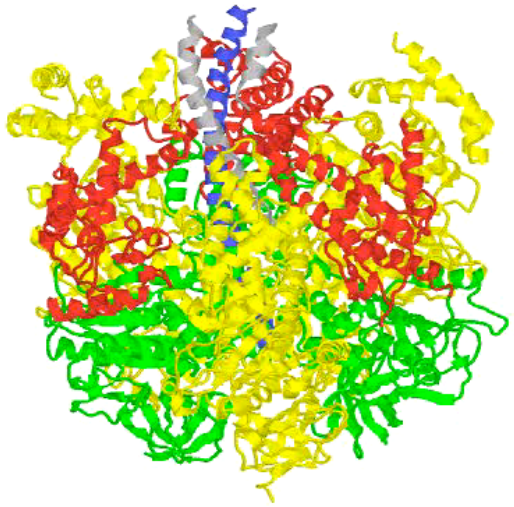
…Crystals of Reduced Dimensionality

H.C. Berg, Rowland Institute
http://www.bmb.leeds.ac.uk/illingworth/motors/flagella.htm

Artificial vs Biomolecular Machines

Structural Information : Order and Dynamics

ATP Synthase



- **Newtonian Mechanics**
- **Rigid parts**
- **Arbitrary sizes and shapes**
- **Joint parts carry no DOF**
- **Structure's Tm >> T**
- **Thermal energy dissipation (vibr) is decoupled from function**
- **States of absolute rest**
- **Need energy for motion and action**

Artificial vs Biomolecular Machines

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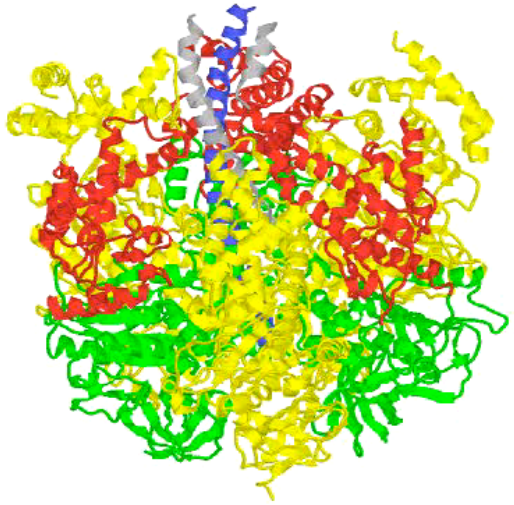
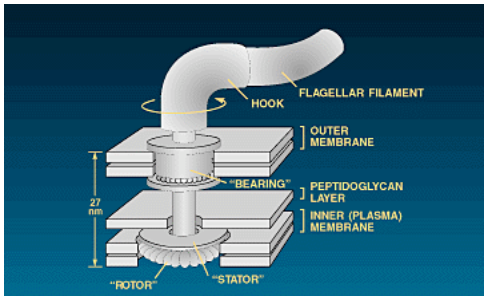


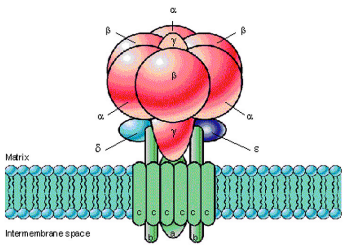
- —Newtonian Mechanics
- —Rigid parts
- —Arbitrary sizes and shapes
- —Joint parts carry no DOF
- —Structure's Tm >> T
- —Thermal energy dissipation (vibr) is decoupled from function
- —States of absolute rest
- —Need energy for motion and action

- —Statistical and Quantum Mechanics
- —Non rigid parts
- —Limited shapes (structural theories)
- —Every part added carries additional DOF's
- —Structure's Tm ≈ T
- —Thermal energy dissipation (vibr, rot, conf, coll.) is part of its function
- —Never "rest" (zero point energies)
- —Need energy to stop (change their state of motion) and action

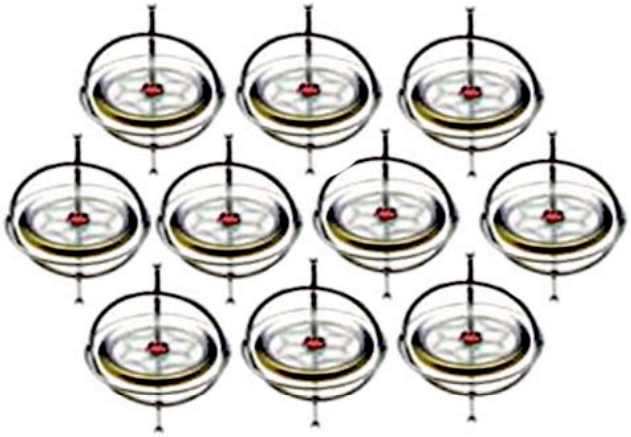
To "engineer" internal dynamics in close-packed systems, emulate structural attributes of macroscopic and biomolecular machines

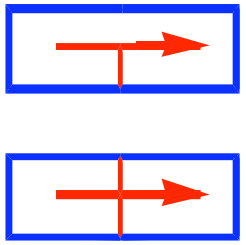
Structurally-Programmed
Volume-Conserving
Correlated
Periodic (Rotary or Oscillatory)

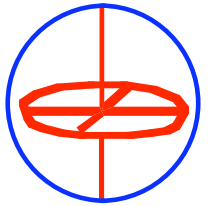


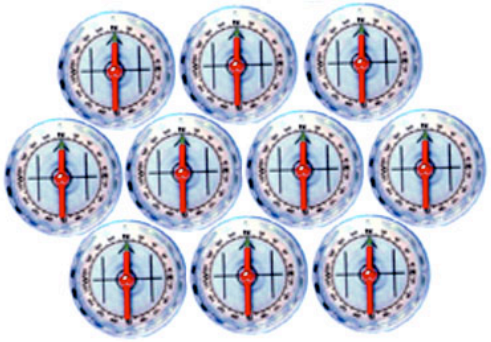


Structurally Programmed, Volume-Conserving Motions







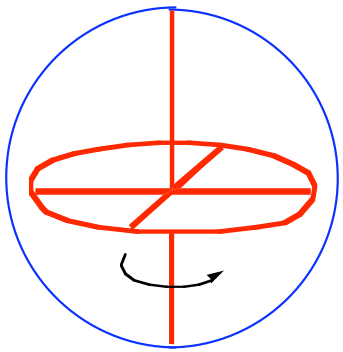


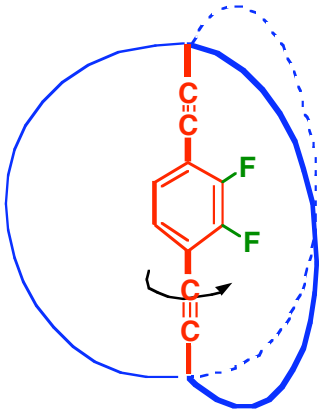
Homeomorphic

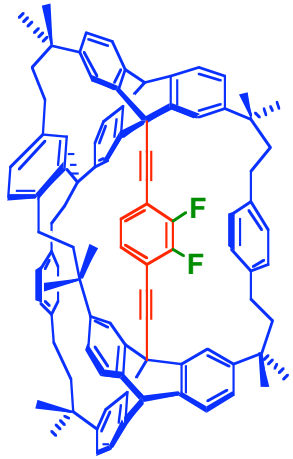
—**"Freely" Rotary or re-orienting element**

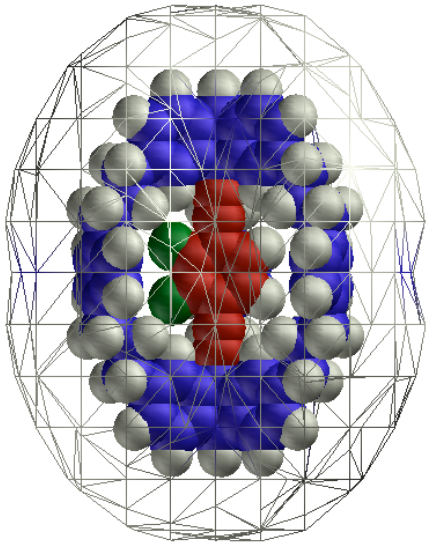
—**Shielding box**

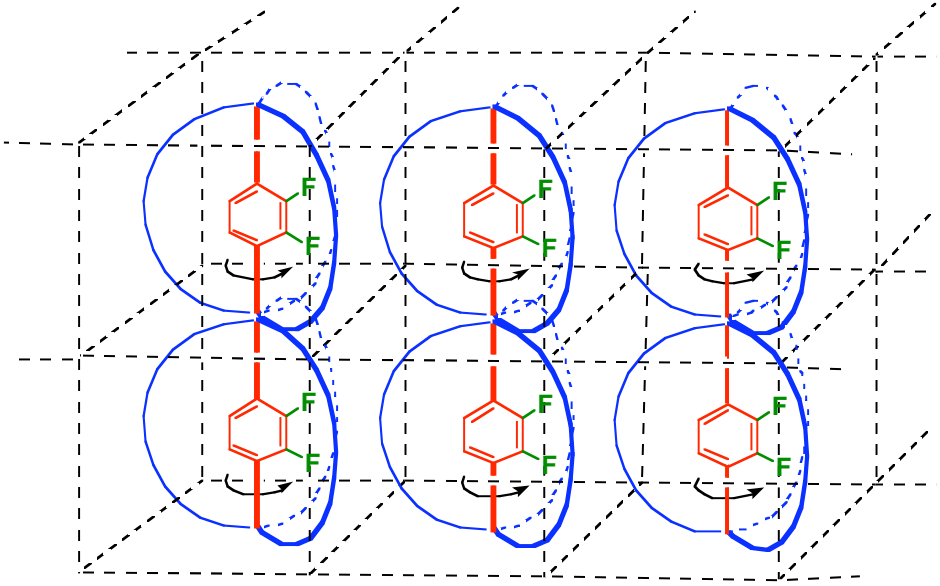
Molecular Compasses and Gyroscopes









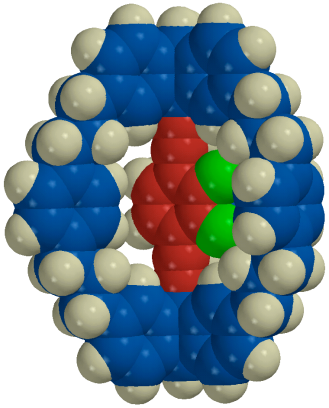


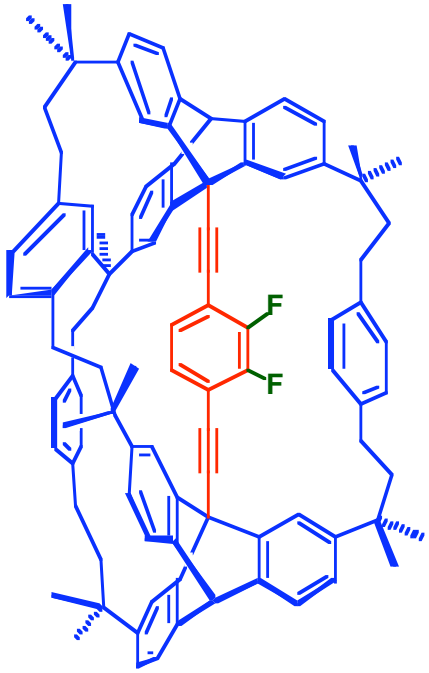
Design Elements (and color code):

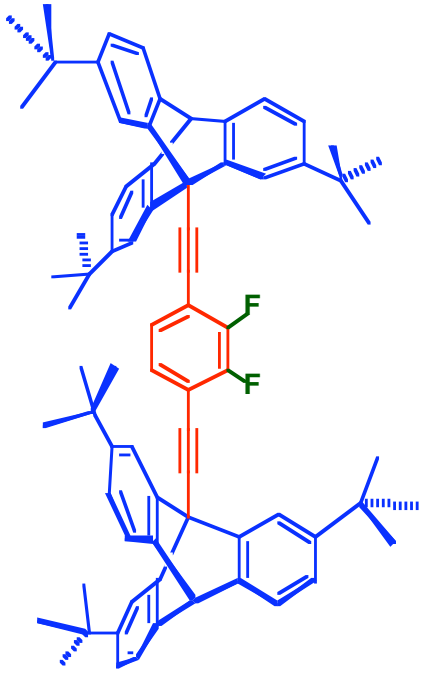
—ROTATOR
(reorienting dipole)
—AXLE
(alkyne linkages)
—STATOR
(shielding groups)

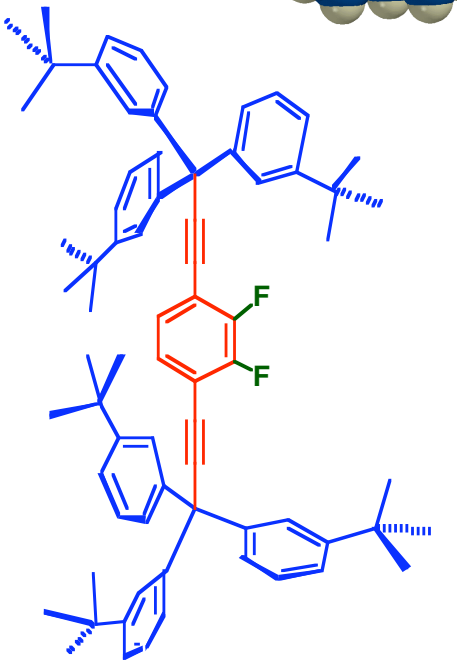
Molecular Compasses and Gyroscopes:

ROTATOR Structures and Topologies





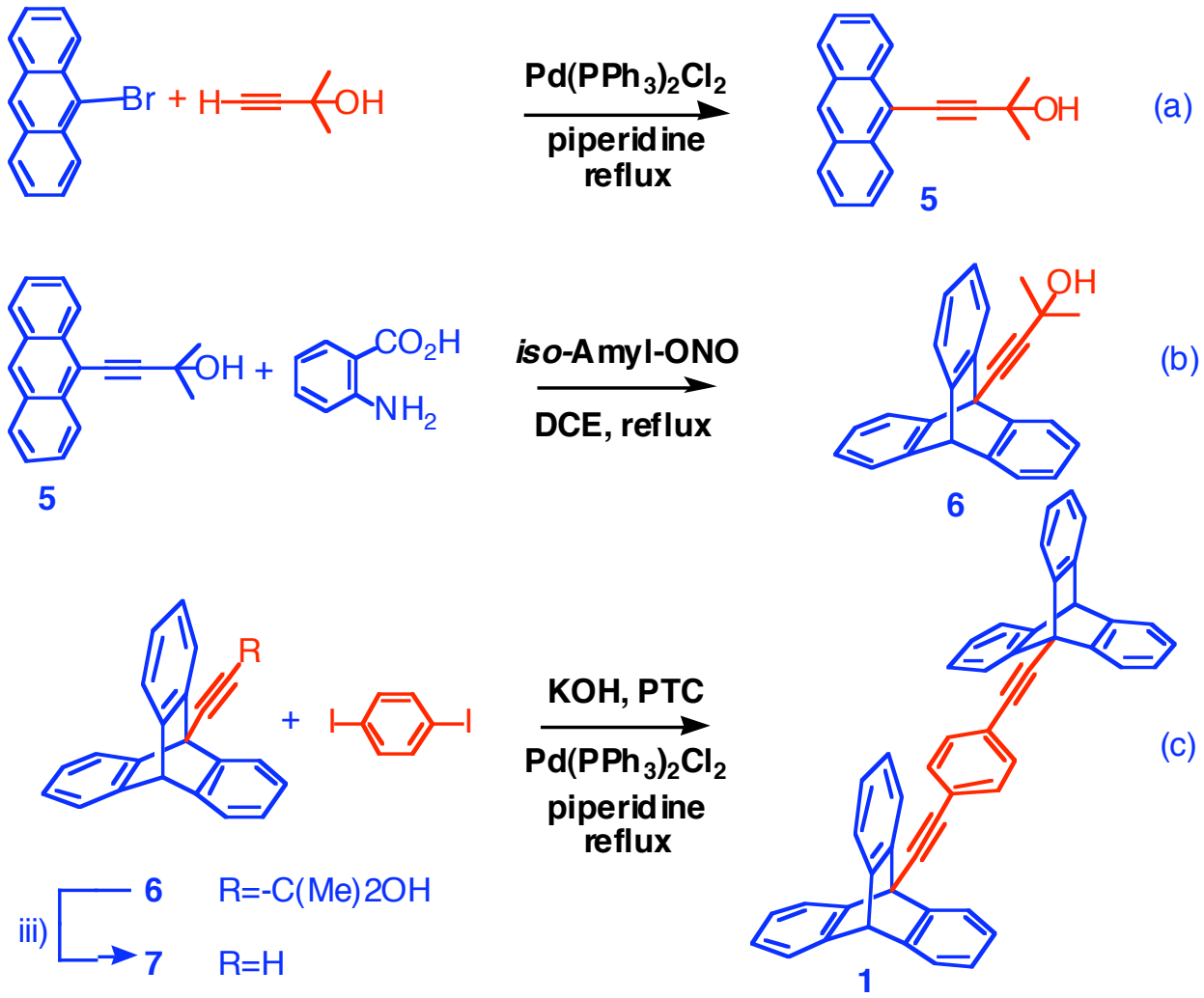




Closed
(triply bridged)

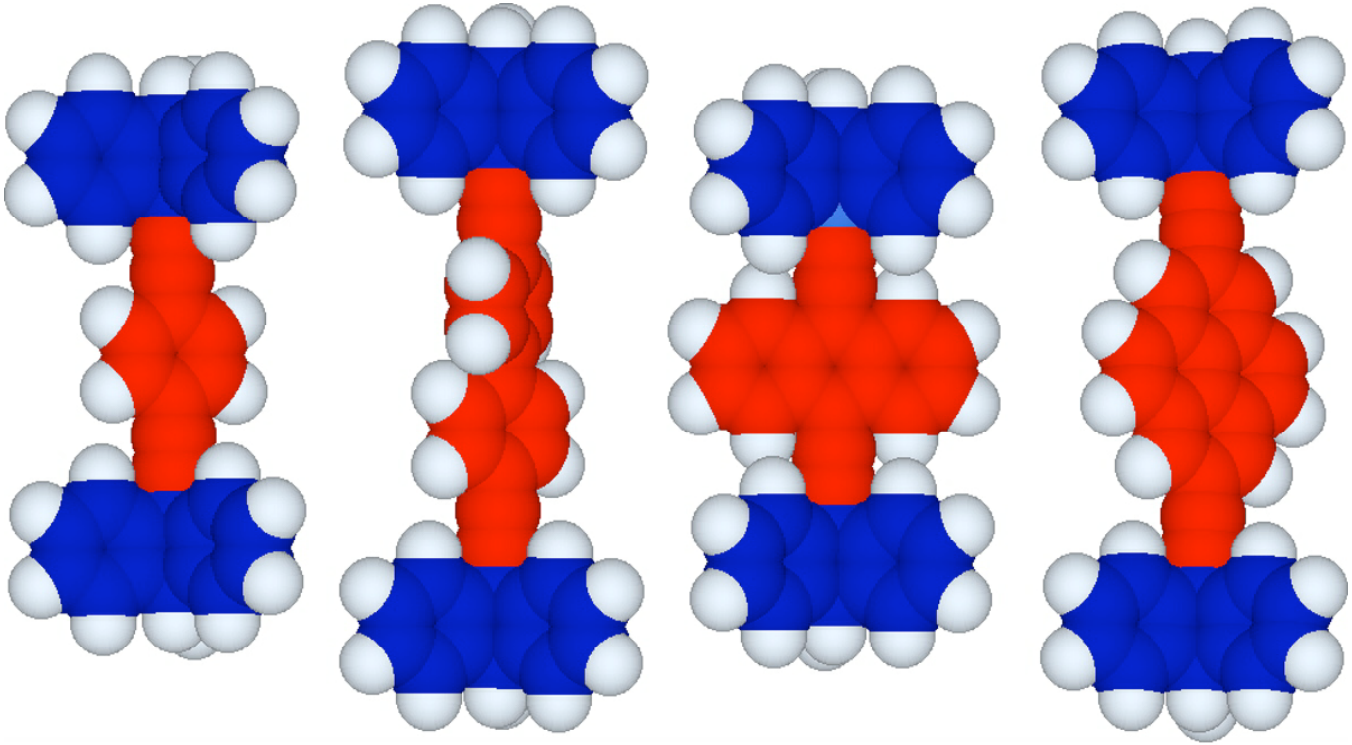
Open
(sterically shielded)

Synthesis of Triptycyl Rotors



Godinez, Zepeda, Garcia-Garibay *JACS*. **2002**, *124*, 4701-4707.

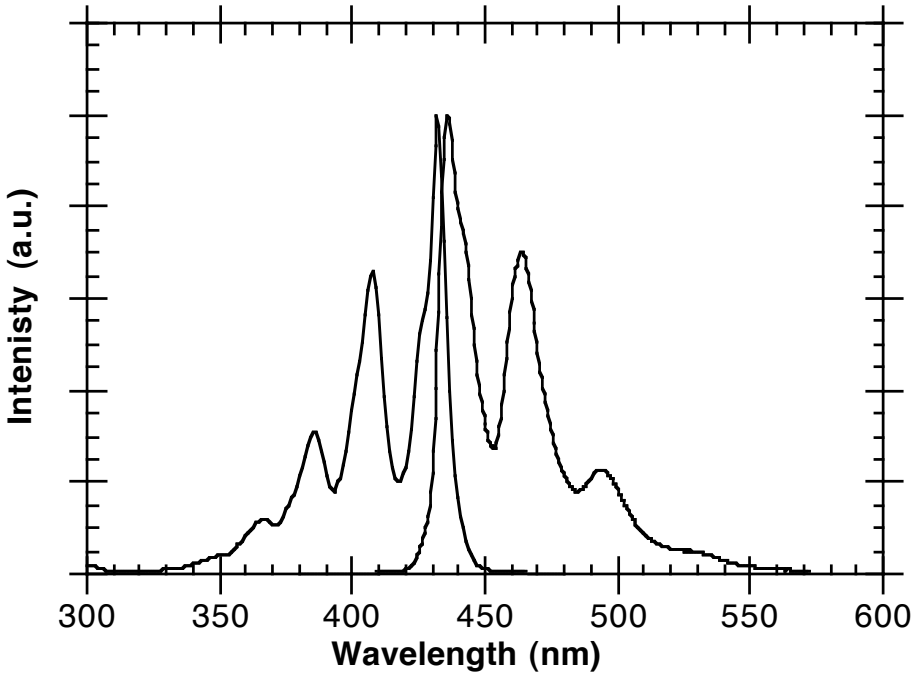
Triptycyl Rotors

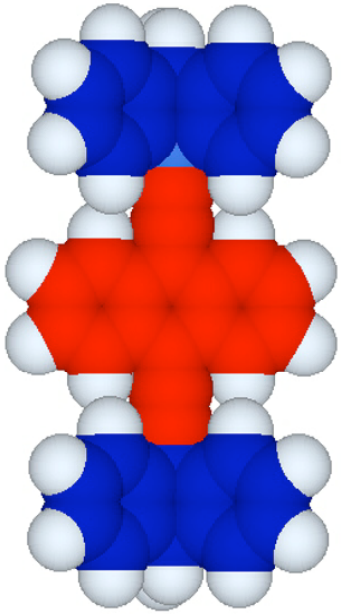


—Insoluble
—Highly Luminescent
—Highly Thermally Stable

Godinez, Zepeda, Garcia-Garibay *JACS*. **2002**, *124*, 4701-4707.

Triptycyl Rotors

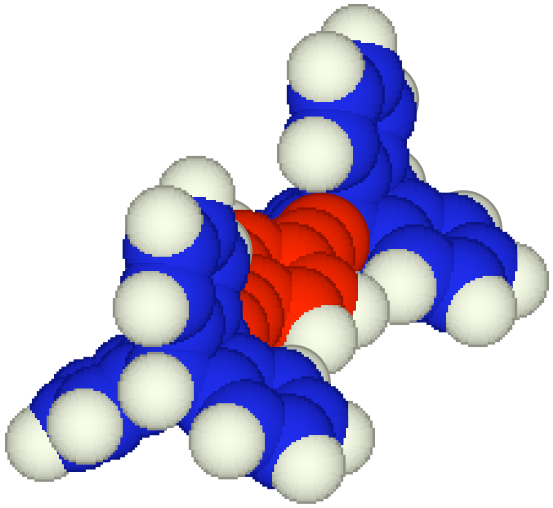


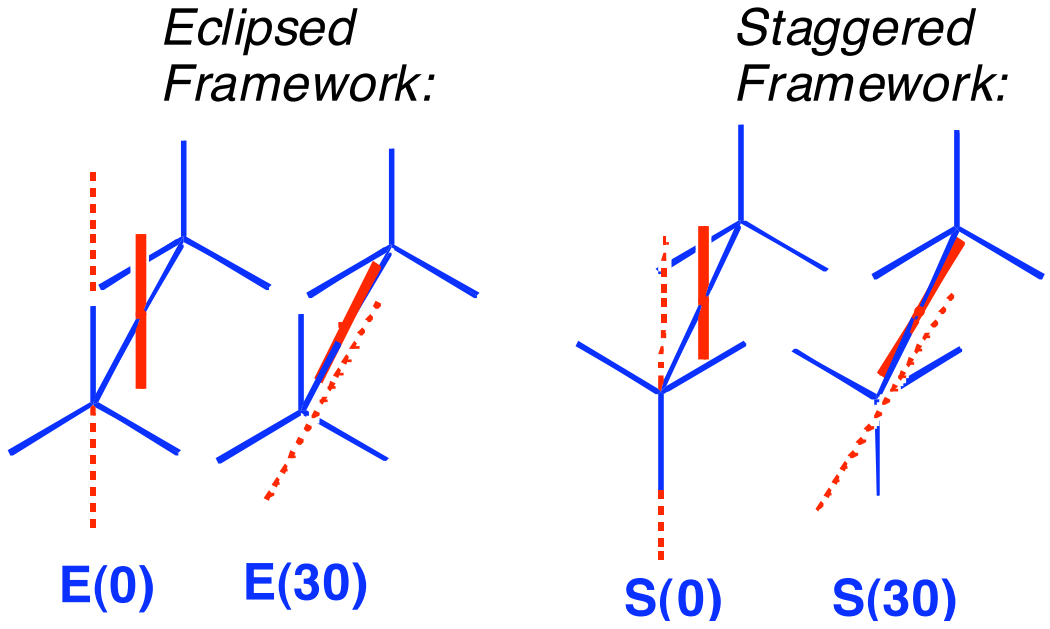


3

Godinez, Garcia-Garibay *unpublished*

Molecular Compasses and Gyroscopes: Internal Rotation

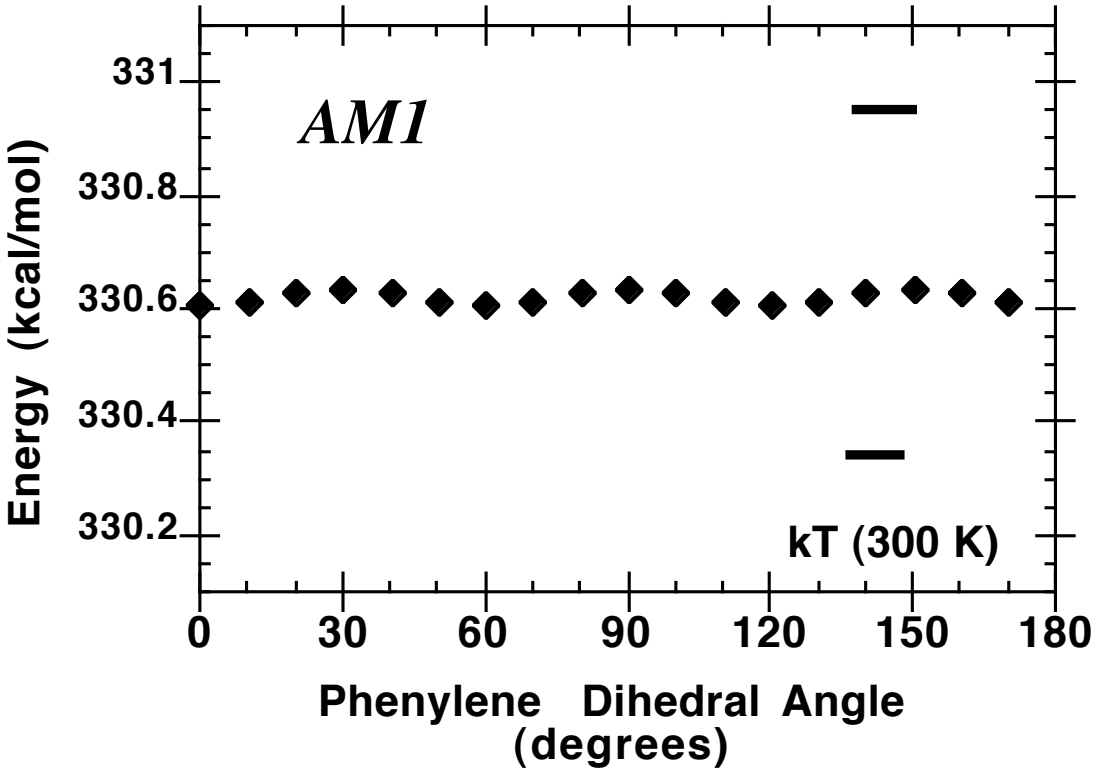


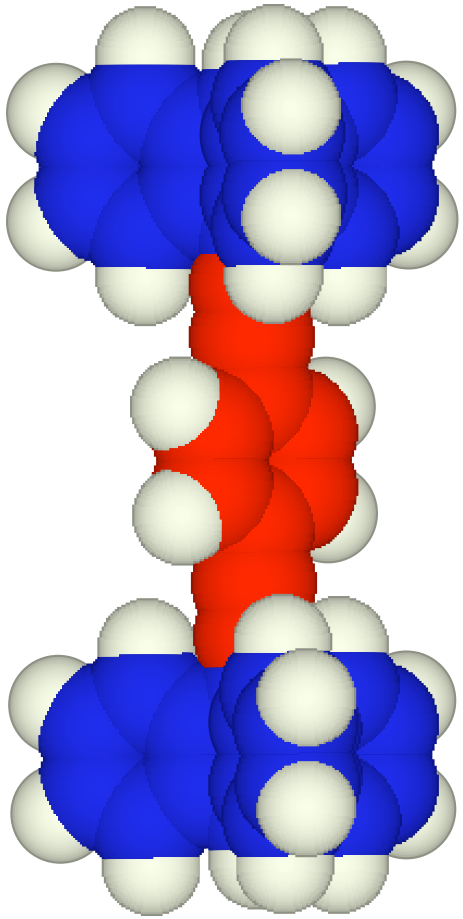


Conformational energy

$E(\phi) \approx S(\phi)$

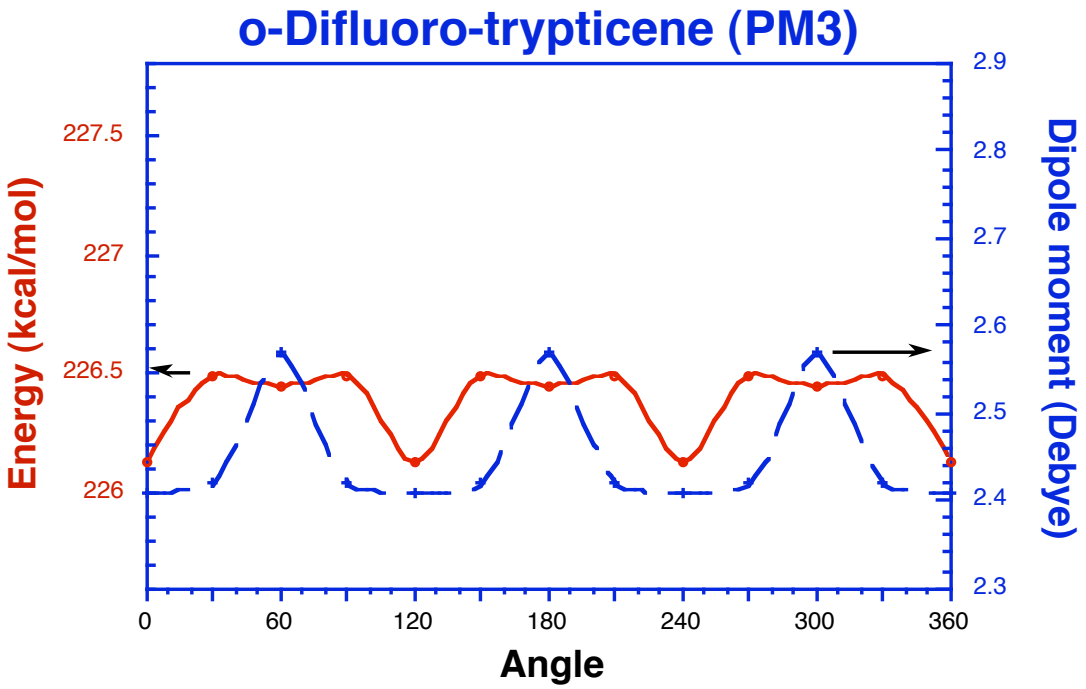
"Free" Rotors

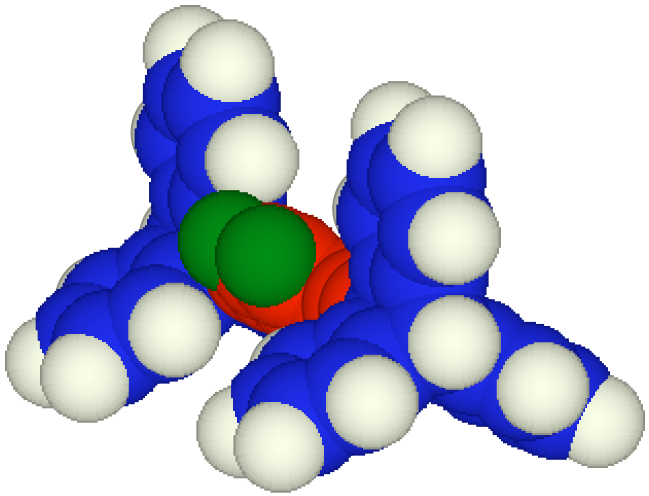




"Free Rotation" about sp-sp^n single bonds:
Saebo et al. *J. Mol. Struct.* **1989**, *200*, 361
Sipachev et al. *J. Mol. Struct.* **2000**, *523*, 1

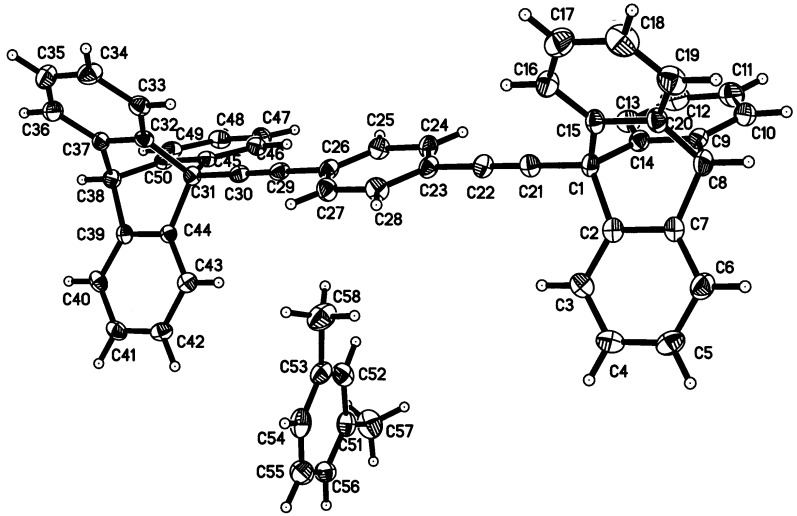
Internal Rotation of Polar Groups

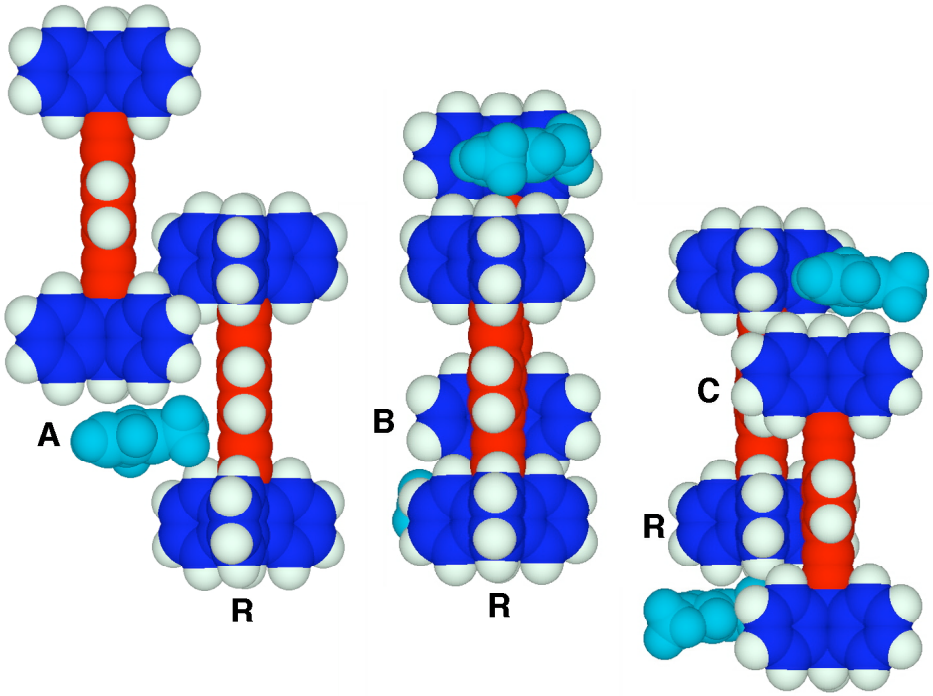




Dipoles change both in orientation and magnitude

Phenylene Rotor Triptycyl Frame



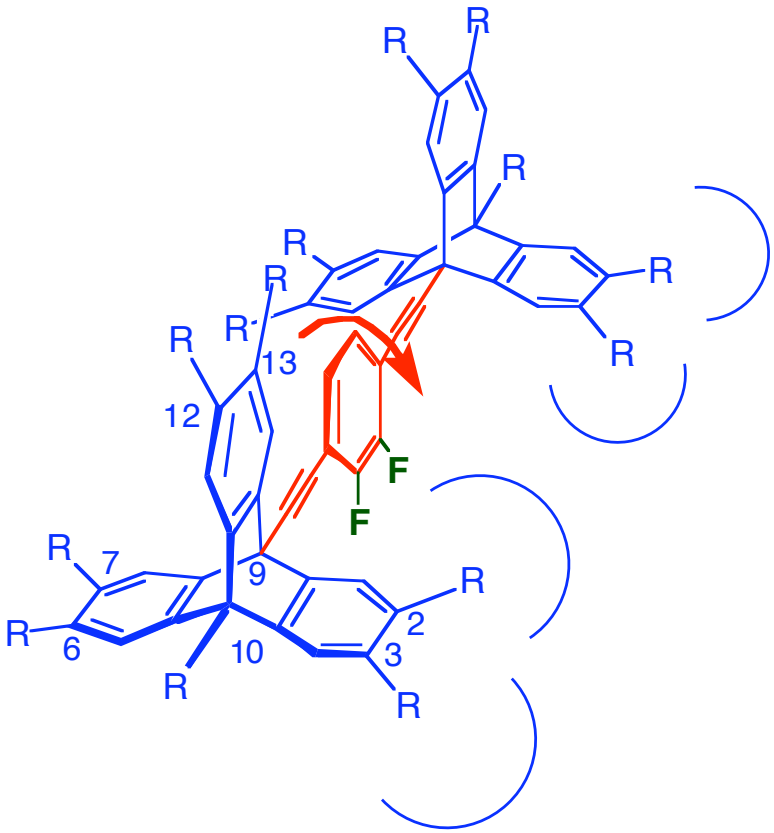


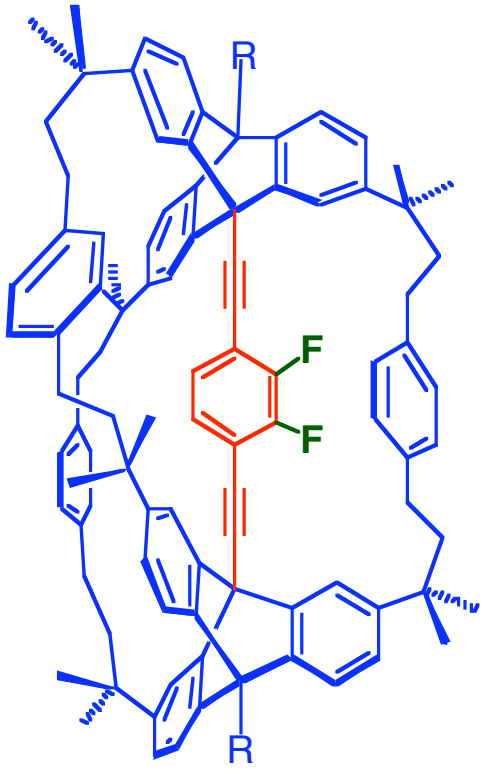
From m-Xylene
$C_{50}H_{30}.C_8H_{10}$
$P_{1\text{-bar}}$
Z=2

- *"Nematic" Like*
- *Interdigitation*
- *Solvent present*
- *Static*

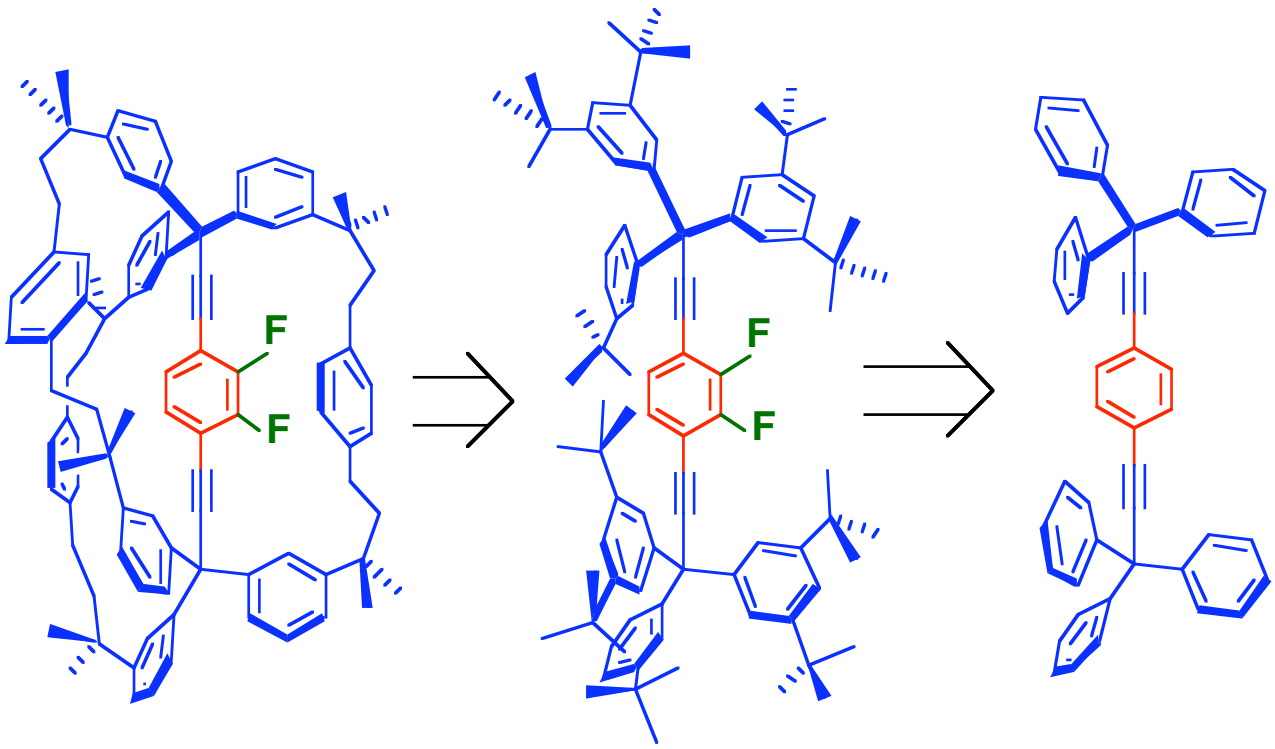
Godinez, Zepeda, Garcia-Garibay *JACS*. **2002**, *124*, 4701.

A Lesson from Triptycyl Frames





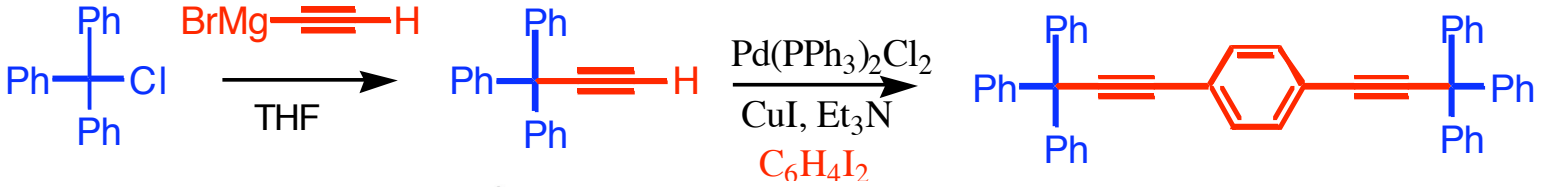
Triphenylmethyl Frameworks

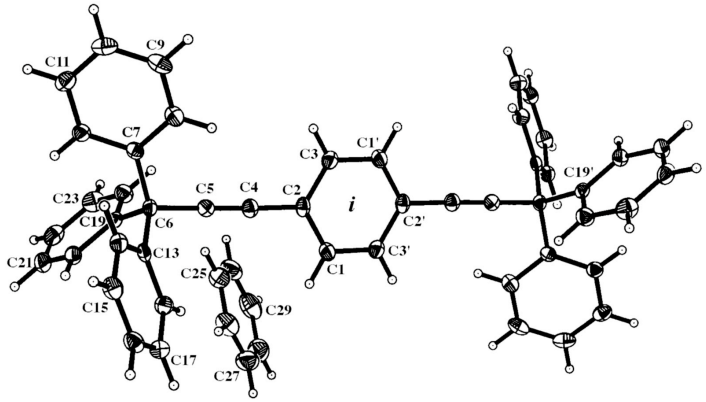


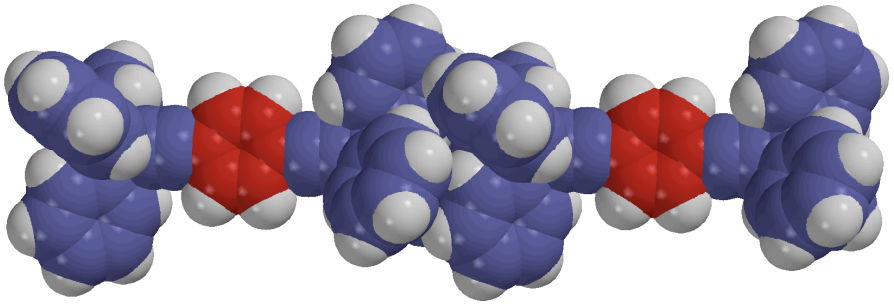
Dominguez, Dang, Strouse and Garcia-Garibay
J. Am. Chem. Soc., **2002**, *124*, 2398

Triphenylmethyl Frameworks

—Convenient Synthesis
—Added degrees of freedom
—Robust Crystals
—Chiral propeller conformations

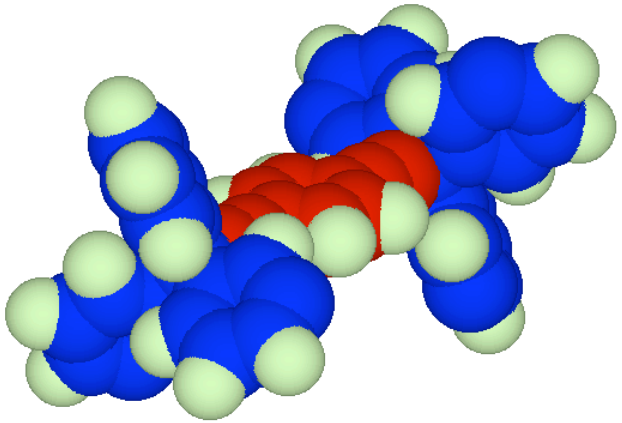


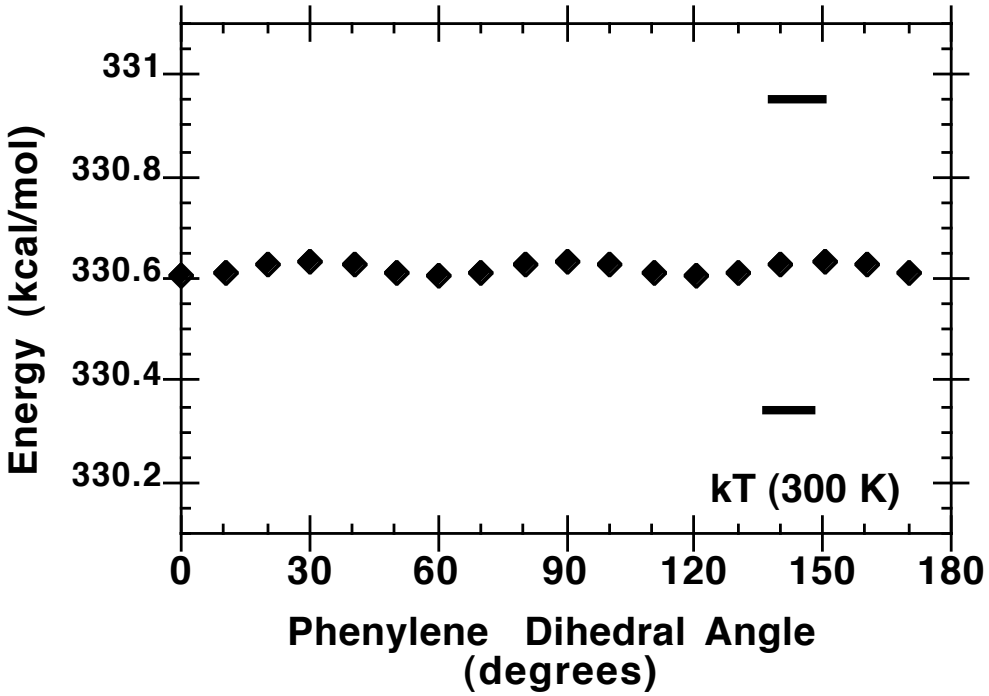




Dominguez et al. JACS, **2002**, *124*, 2398

Gyroscopic Rotation in the Gas Phase (AM1 Method)



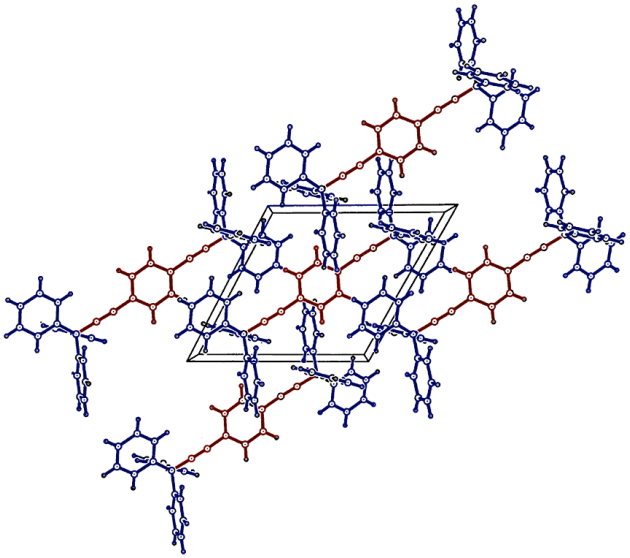


"Free Rotation" about sp-sp^n single bonds:

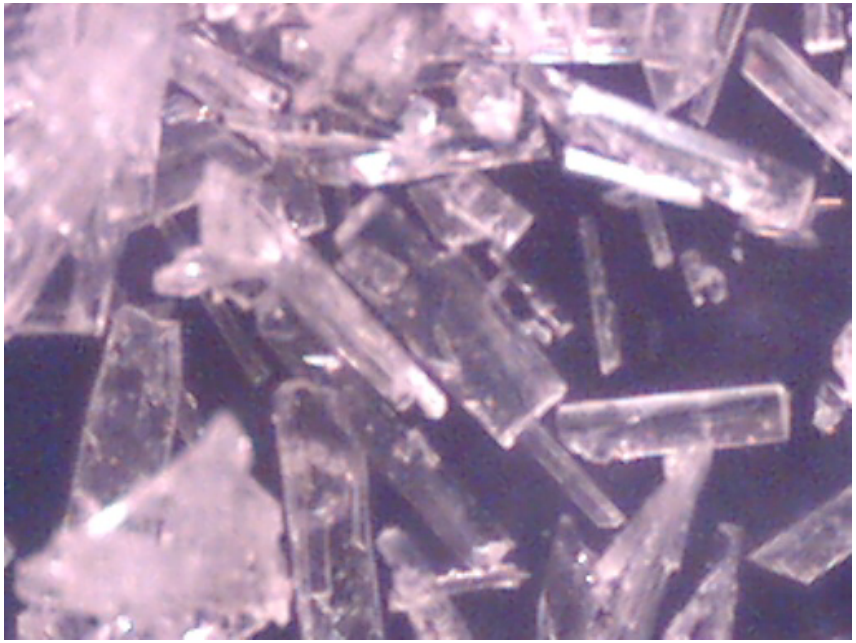
Saebo et al. *J. Mol. Struct.* **1989**, *200*, 361

Sipachev et al. *J. Mol. Struct.* **2000**, *523*, 1

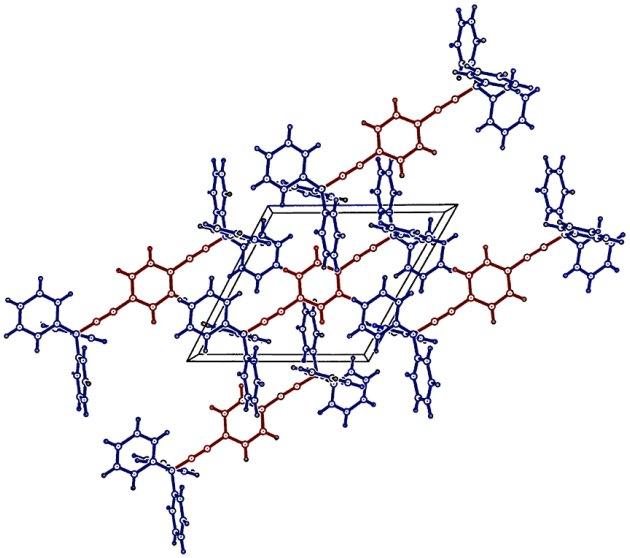
Gyroscopic Rotation in Crystals?



-No Diffusion
-No Rotation
-Few Conformational Motions



Gyroscopic Rotation in Crystals?



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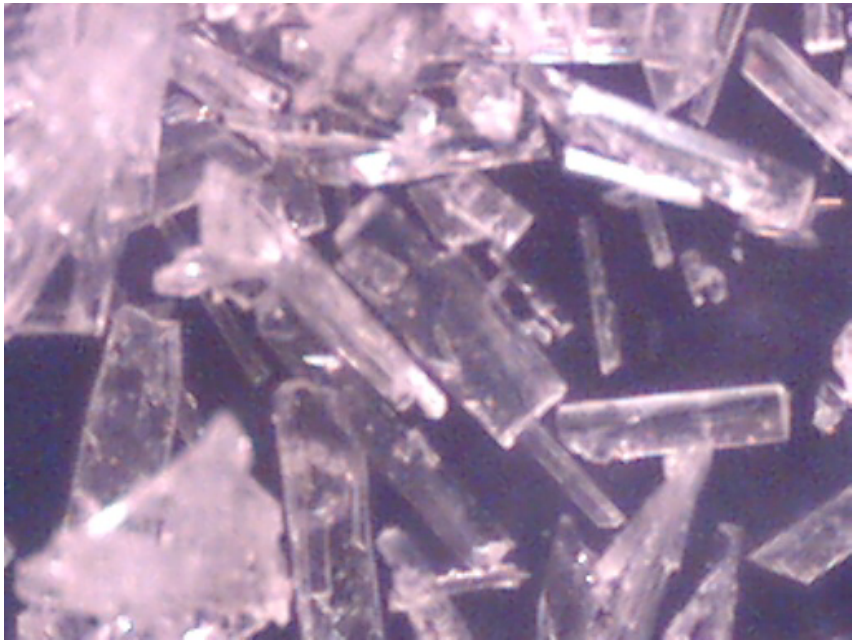
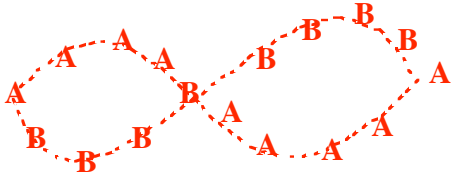


Crystal Dynamics?

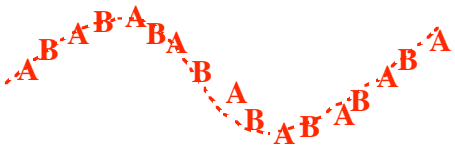
Phonons:

STATIC: A B A B A B A B A B A B A B A

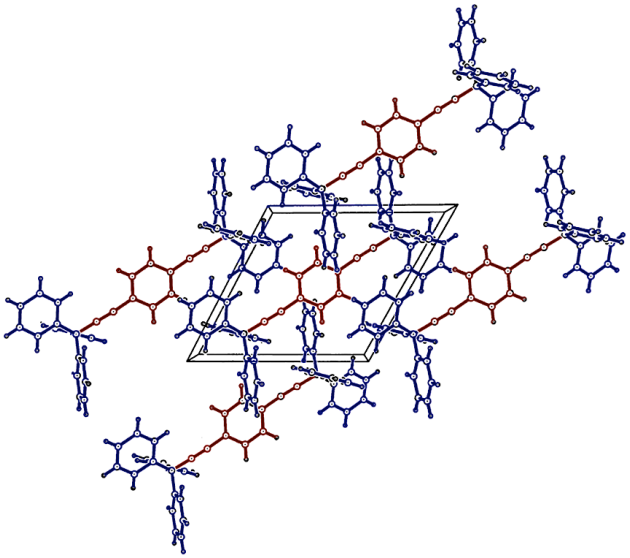
OPTICAL PHONONS



ACOUSTIC PHONONS



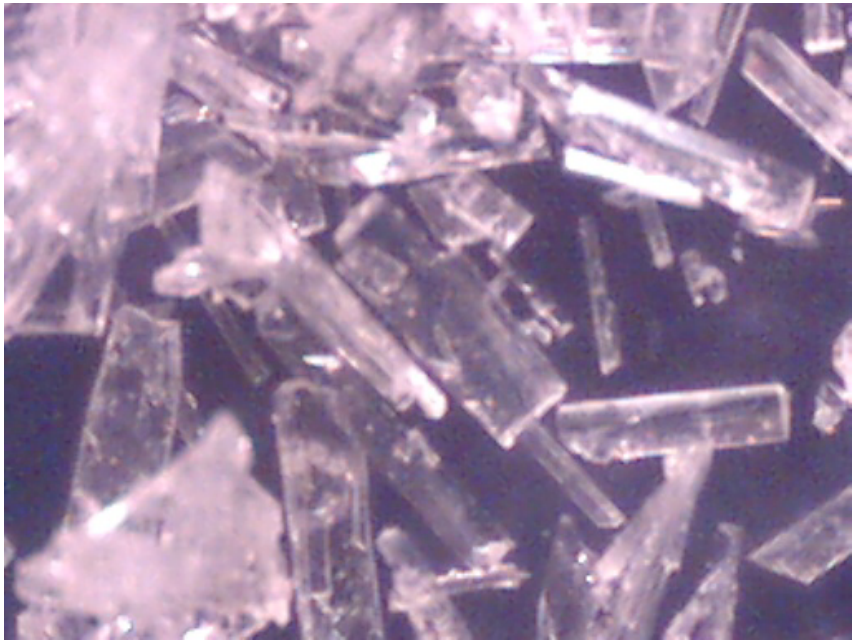
Gyroscopic Rotation in Crystals?



-No Diffusion

-No Rotation

-Few Conformational Motions

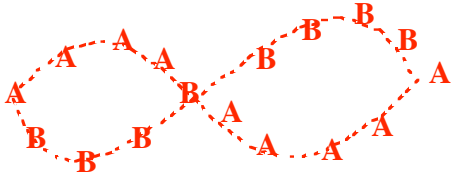


Crystal Dynamics?

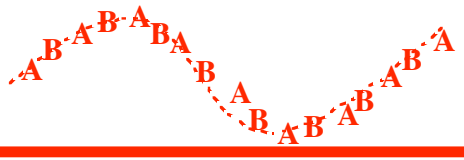
Phonons:

STATIC: A B A B A B A B A B A B A B A

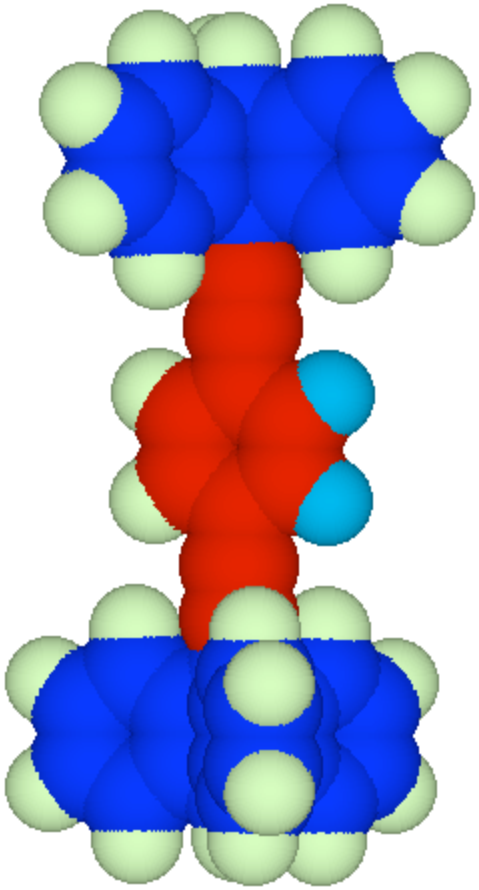
OPTICAL PHONONS



ACOUSTIC PHONONS



Gyroscopic rotation result from coupled motions



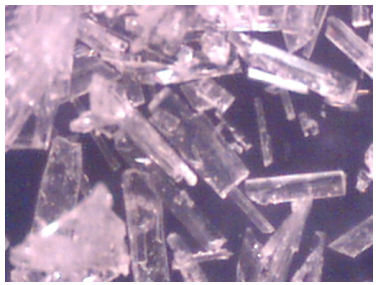
Inertial Rotation :

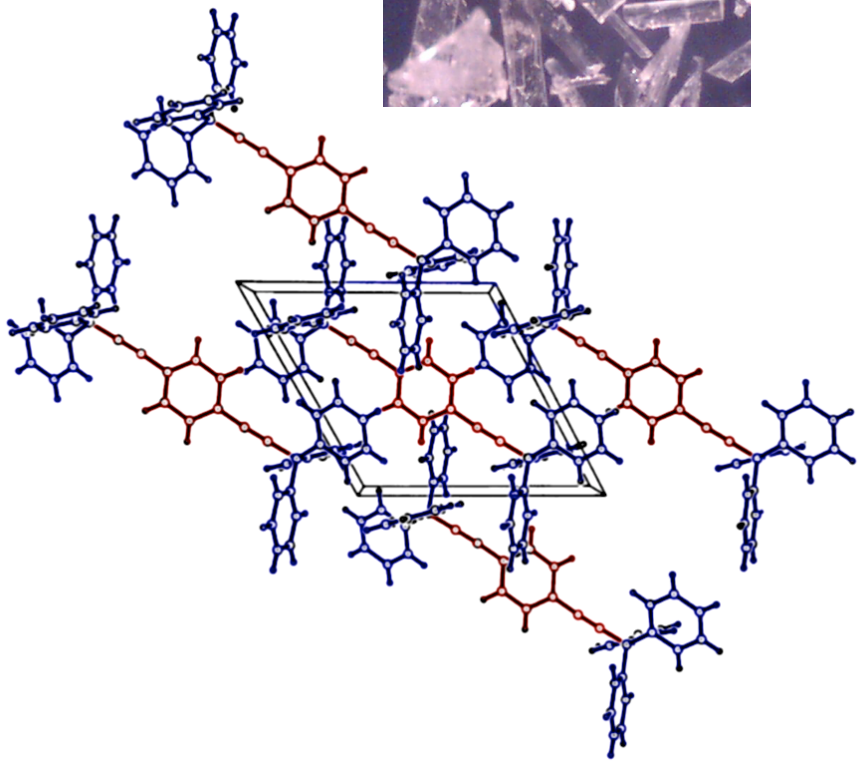
τ_{FR}^{-1} = 2.4 x 10^{12} sec^{-1} at 298 K

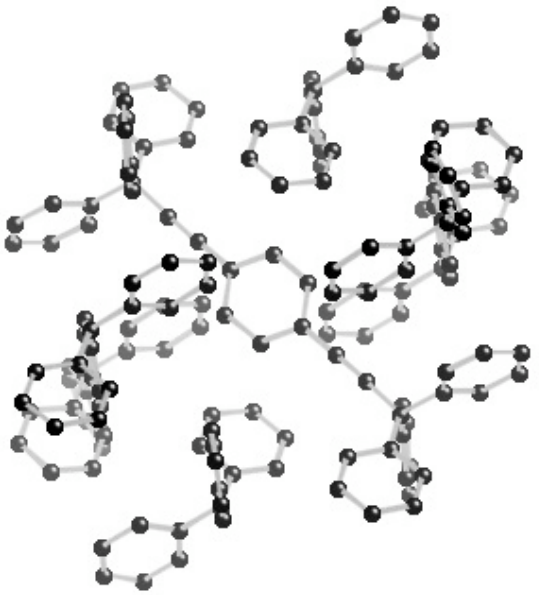
[$\tau_{FR} = (2\pi / 9)\ (I/kT)^{1/2}$]

I= moment of inertia of the 1,4-phenylene with respect to the 1,4-axis

Rotation in the Solid State







Force-Field Model
—Ea ≈ 13 kcal/mol

Experiment (^{13}C, ^{2}H NMR, and dielectric spectroscopy)
—Ea ≈ 12-14 kcal/mol