UCLA

Amphidynamic Materials — Part II

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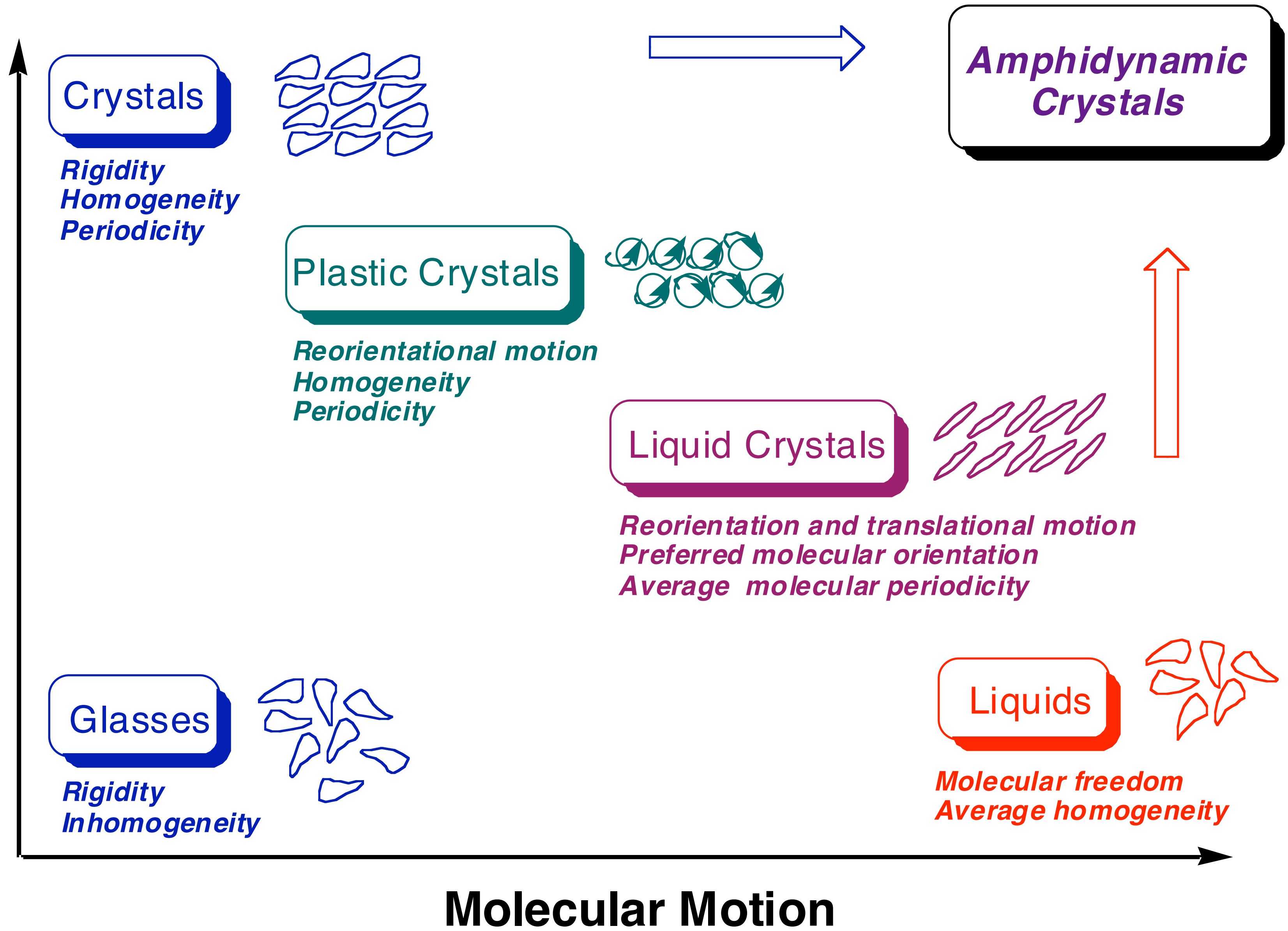
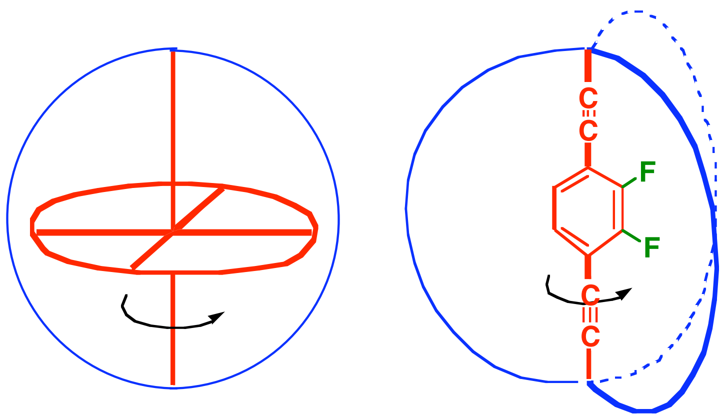
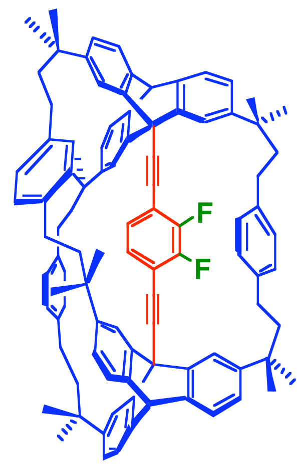
National Science Foundation

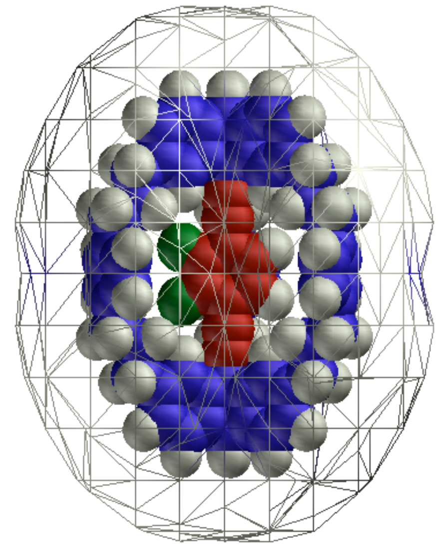
Condensed Phase Matter and Molecular Dynamics

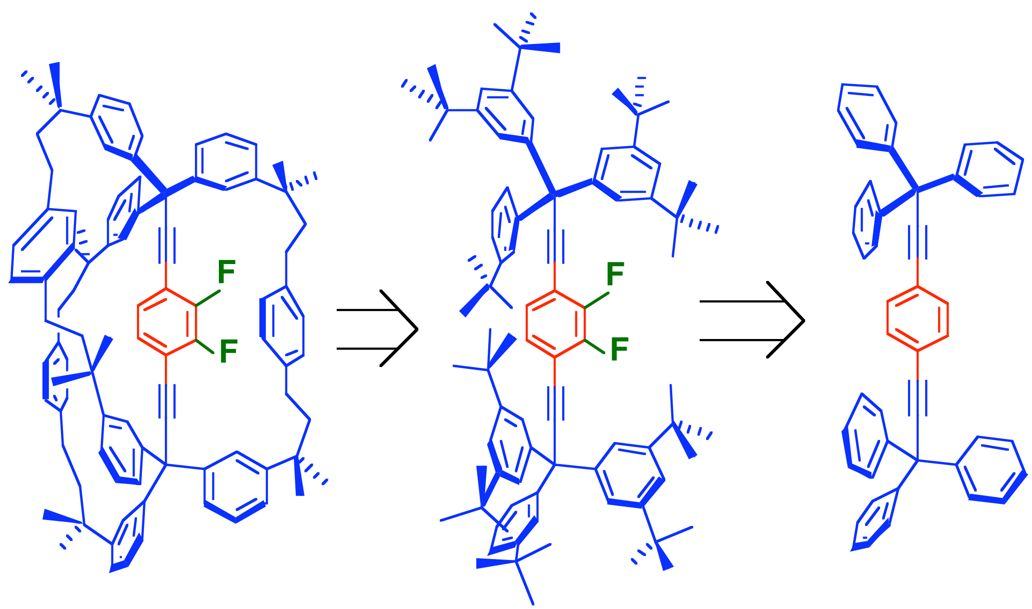


Molecular Compasses and Gyroscopes









Gyroscopic Motion in Crystals

Solid State NMR

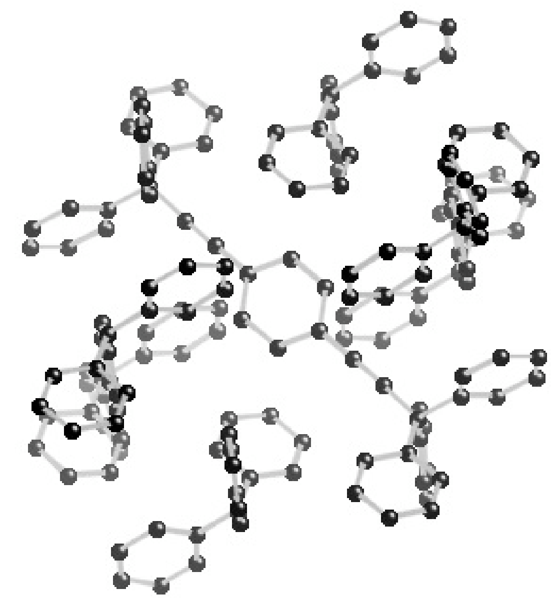
X-Ray Diffraction

Dielectric Spectroscopy

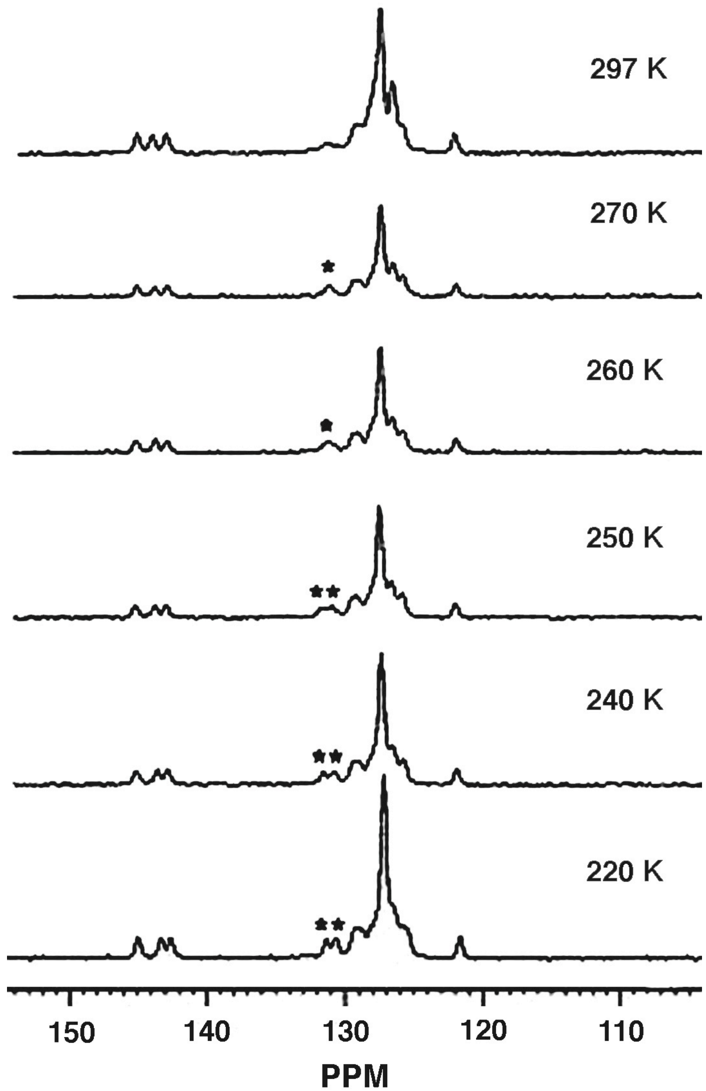
Computer Modeling

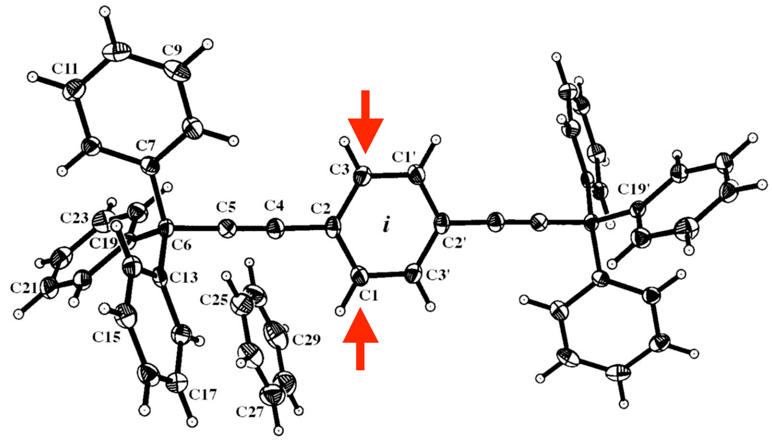
Fluorescence Anisotropy Decay

Inelastic Neutron Scattering

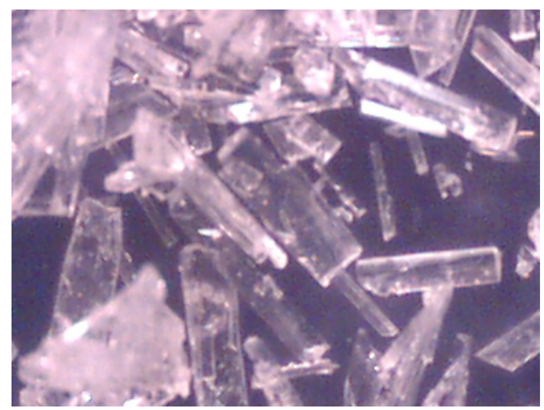


Dynamic NMR: VT ^{13}C CP-MAS



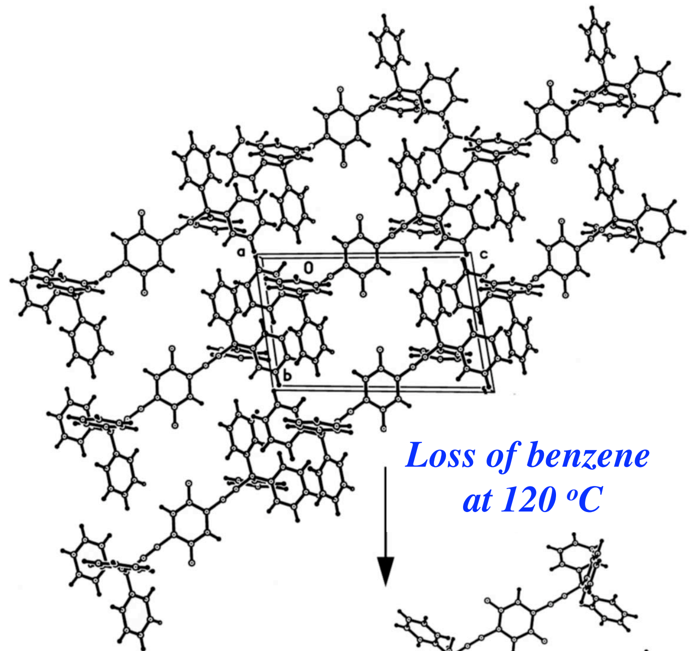


□□ = 60Hz
T_C = -16 ^{o}C
k_{rot} = 267 s^{-1}
Ea = 12.8 kcal/mol



at T_C: k_{exch} = k_{Rot} = □ □□(2)1/2
Ea = RT_C [22.96 + Ln (T_C / □□)]

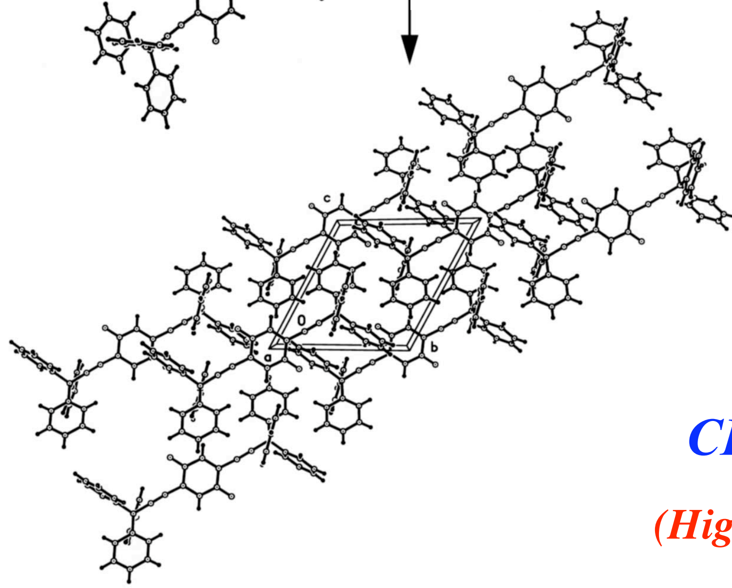
Two Pseudopolymorphs



C_6H_6

(Low Temp)

Loss of benzene at 120 ^oC

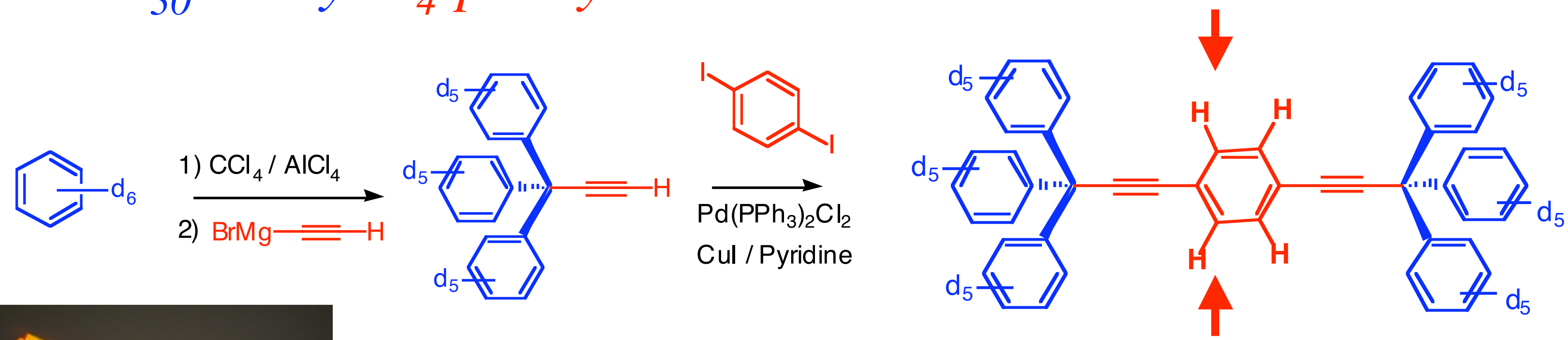


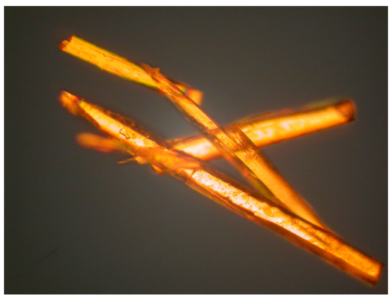
CH_2Cl_2

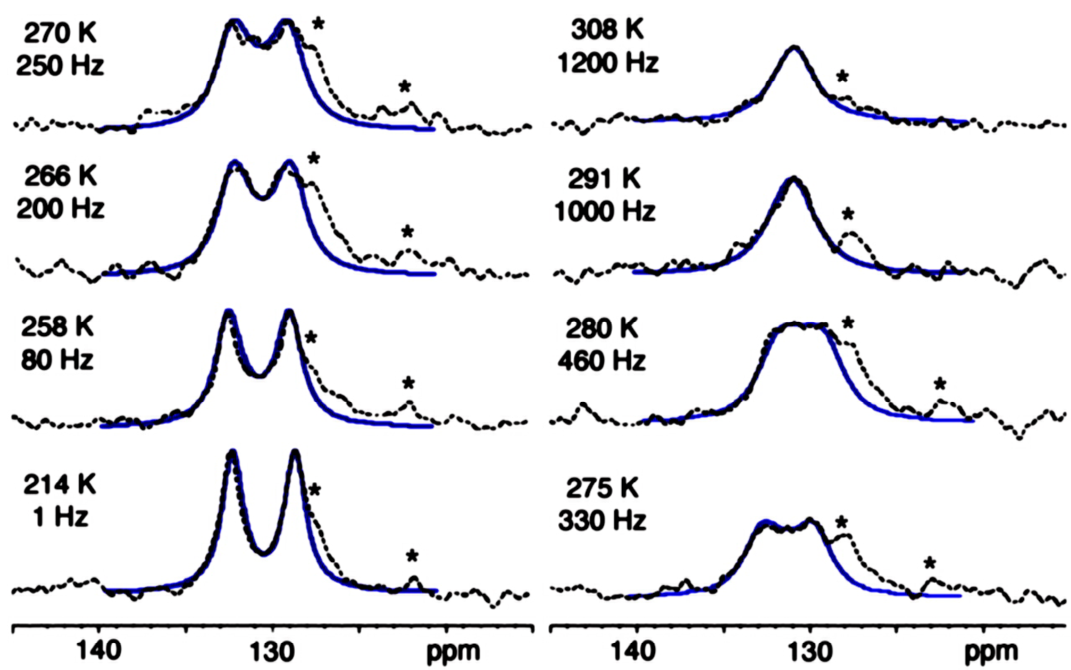
(High Temp)

Solid State Dynamics

d_{30}- Trityl-h_4-phenylene







k_{280} = 611.6 Hz

$\square_a$ = 12.8 kcal/mol

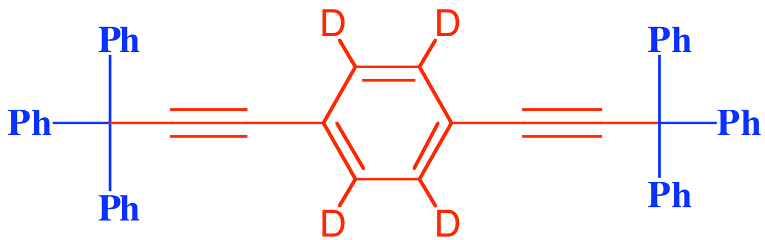
Faster rotation needs heating…
and a different method of measure!

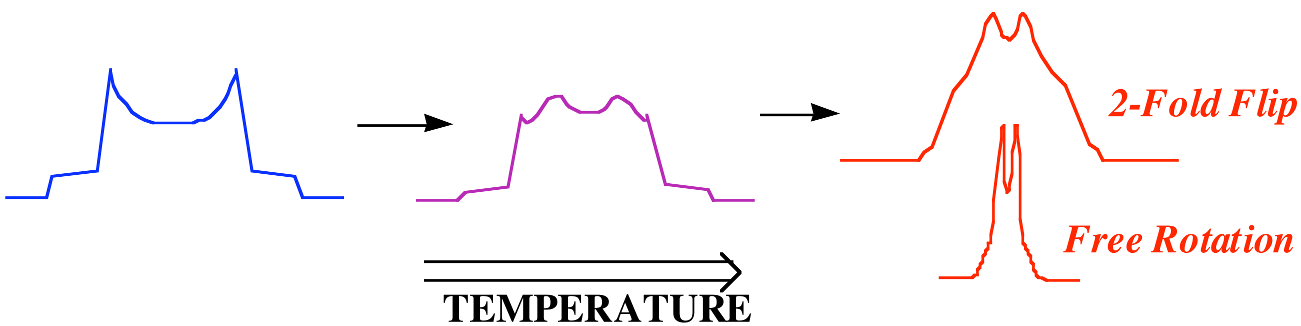
Steve Karlen

Solid State Dynamics

^{2}H NMR Line Shape Analysis (10^4 - 10^8 s^{-1})

$$2\nu_Q = (3/4)(e^2q_{zz}Q/h)\,[\,(3\cos^2\theta-1) + \eta\,\sin^2\theta\,\cos^2\phi)$$



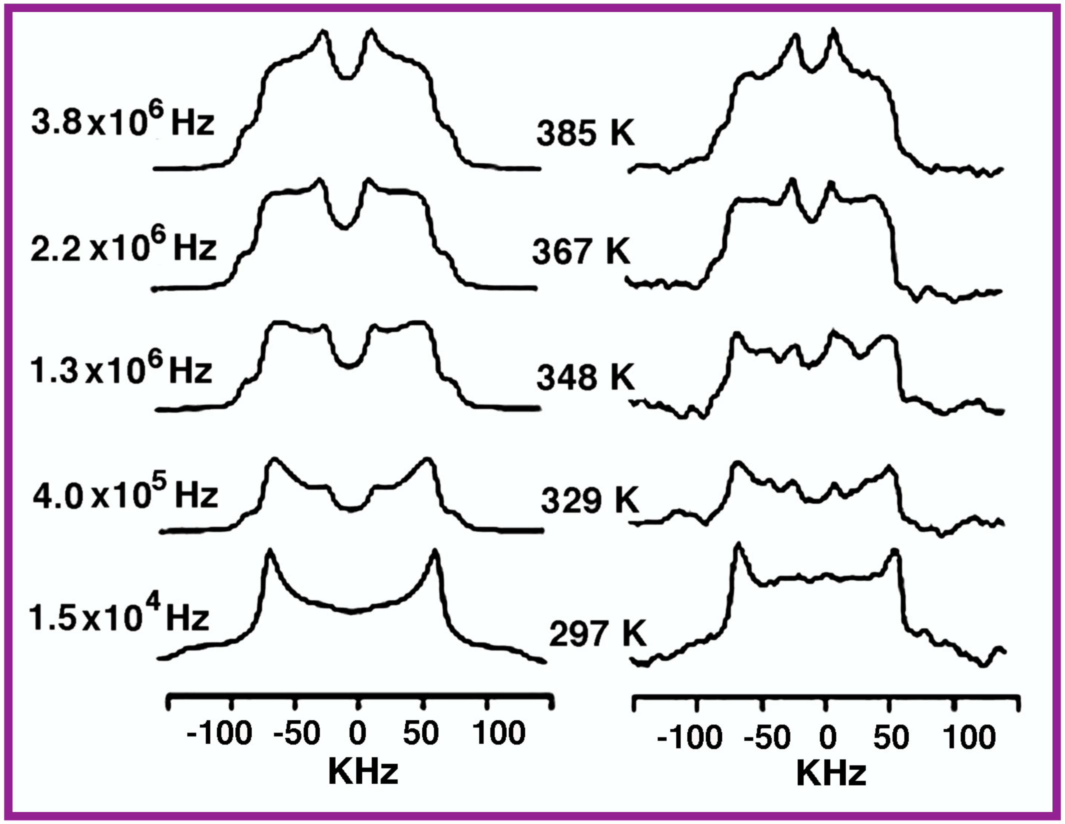


Dynamic averaging of the orientation-dependent interaction between the ^{2}H nuclear spin and the electric field gradient at the nuclear position.

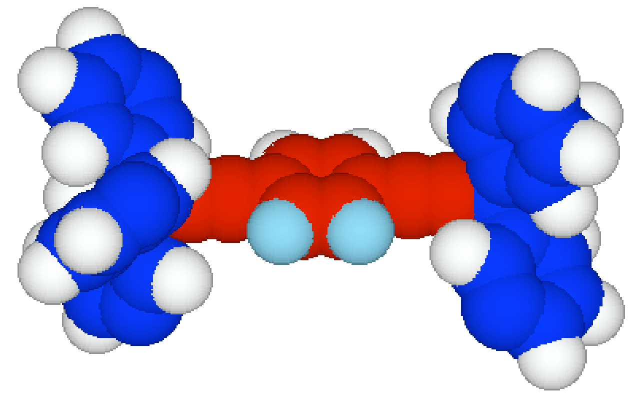
Solid State Dynamics by ^{2}H NMR

^{2}H NMR

Calculated *Experimental*



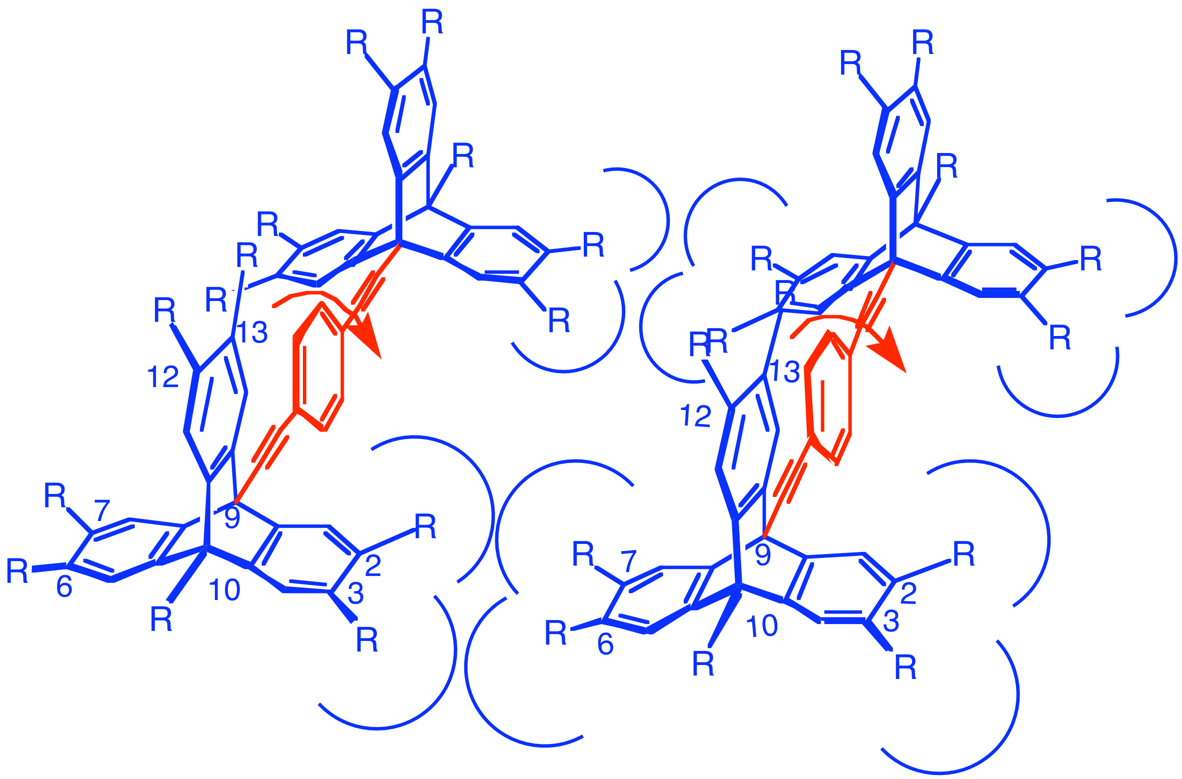
Two-fold flip (X-ray structure)



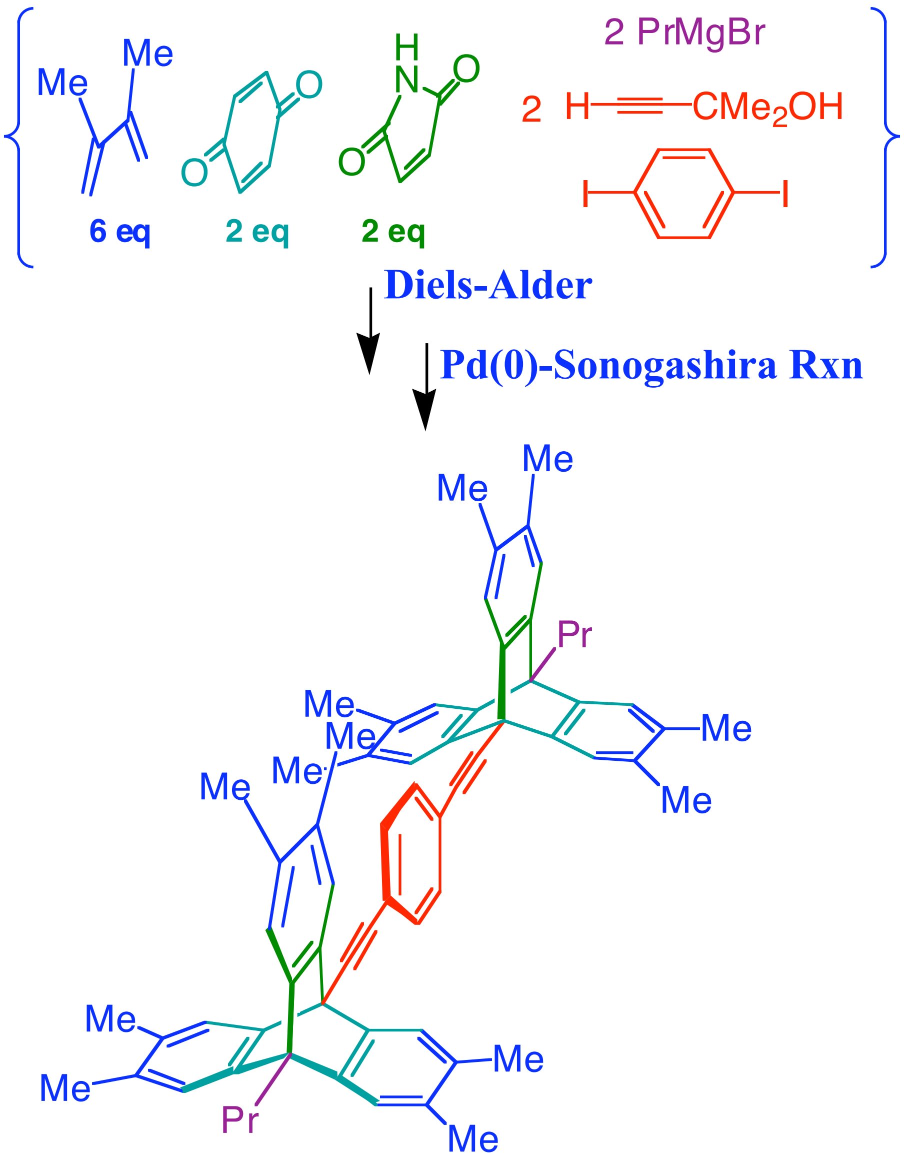
1.3 MHz Rotation by 75 °C !

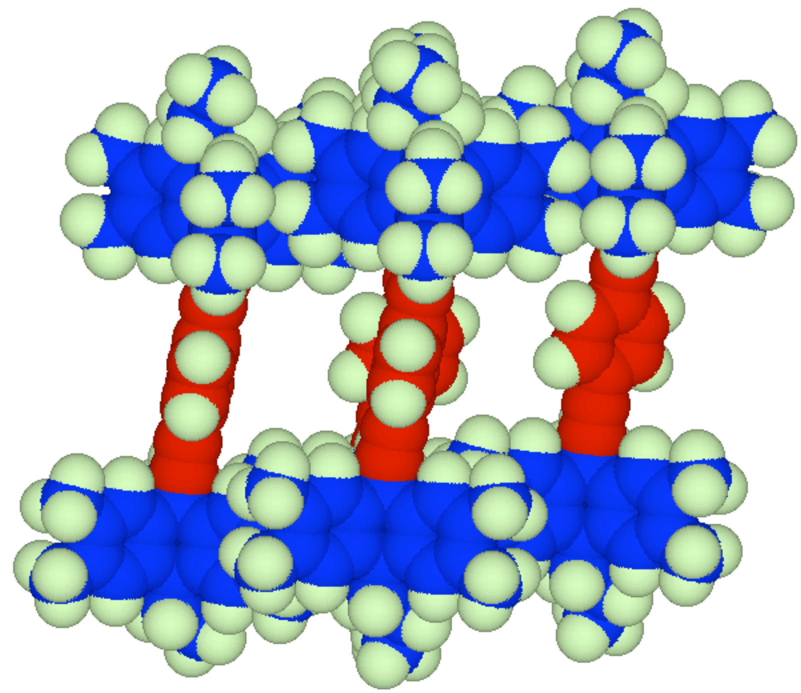
Two-fold flip
Ea = 14.6±1.5 kcal/mol

A Robust Frame for Robust Crystals



Robust and Shielding Triptycyl Frames



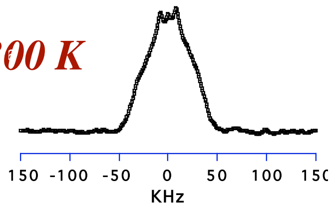


Cl-Benzene Removed

Godinez et al. J. Org. Chem. 2004, 69, 1652.

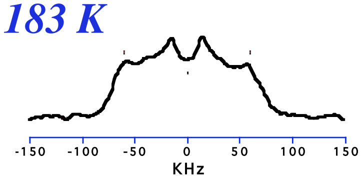
^{2}H NMR Line Shape Analysis

300 K

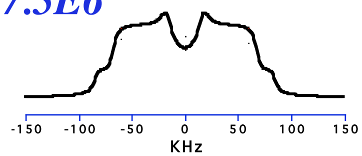


Too narrow to fit a 2-fold flip, but no continuous rotation

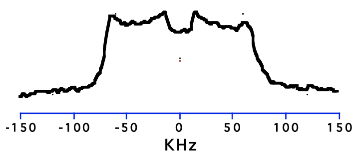
183 K



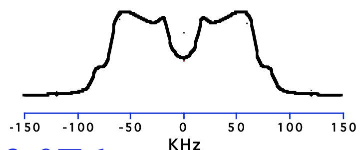
7.5E6



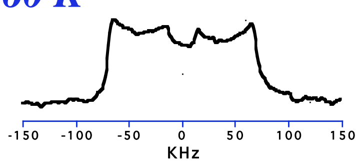
173 K



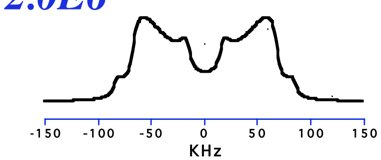
4.5E6



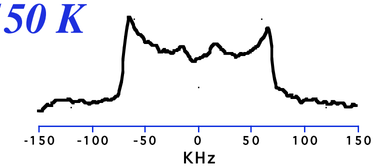
160 K



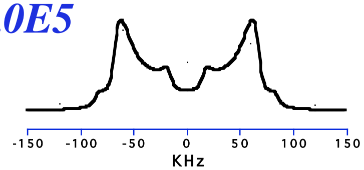
2.0E6

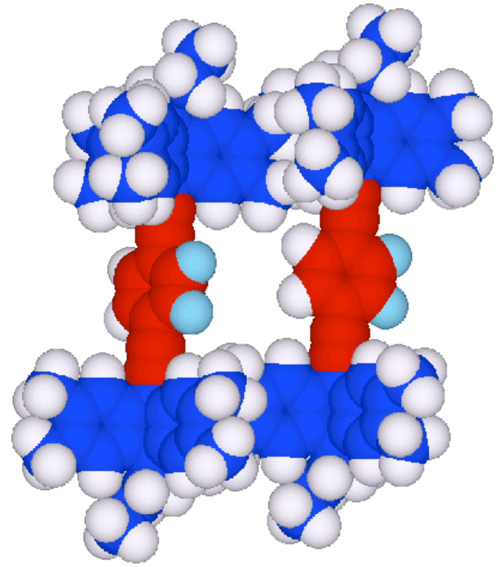


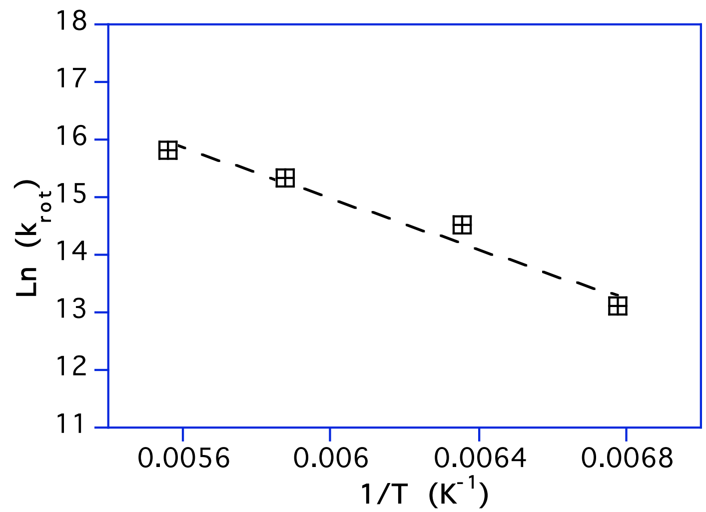
150 K



5.0E5







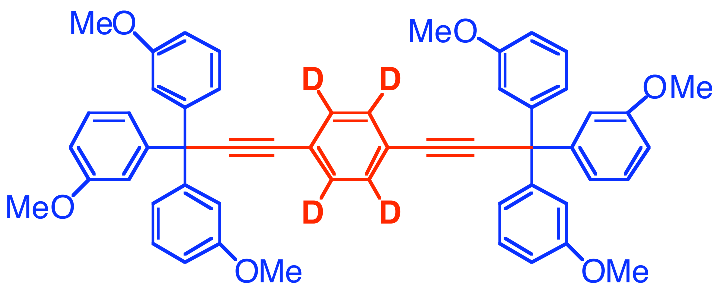
$A = 1.45 \times 10^{12}$; $Ea = 4.3$ kcal/mol

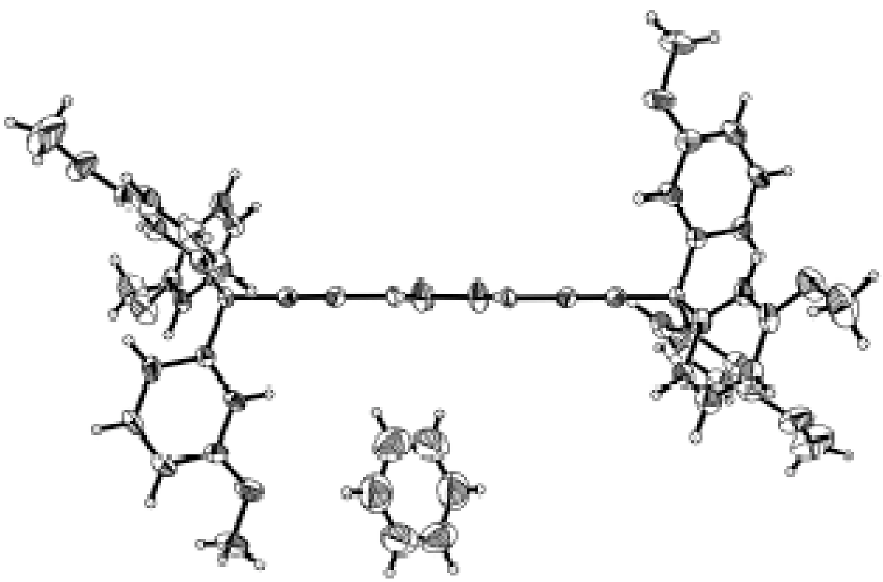
Godinez et al. unpublished

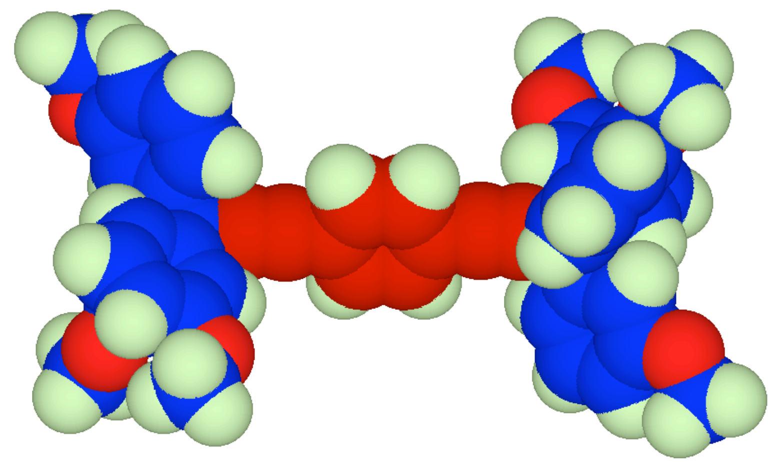
Rotational Dynamics by X-Ray Diffraction

Dunitz, J.; Maverick, E. F.; Trueblood, K. N.

Angew. Chem. Int. Ed. 1988, *27*, 880-895.





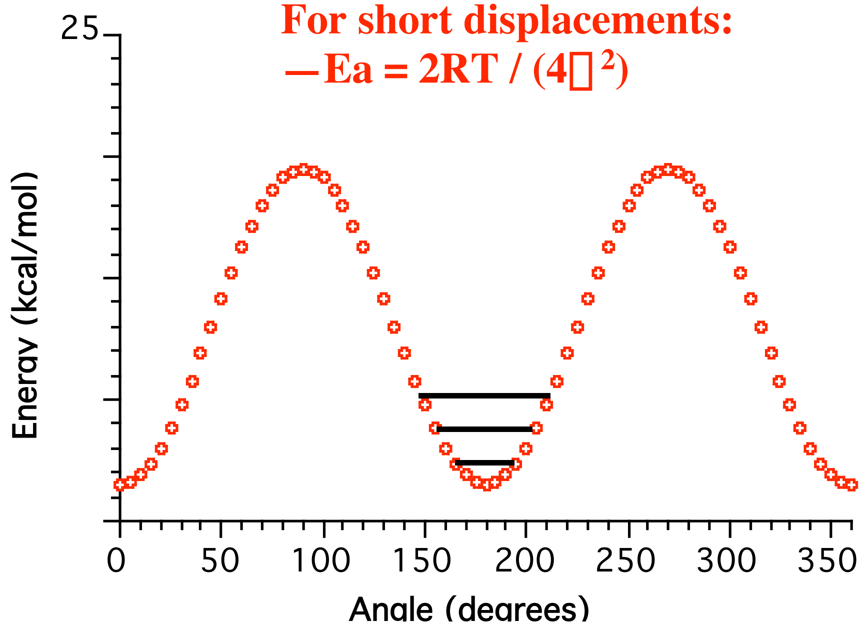


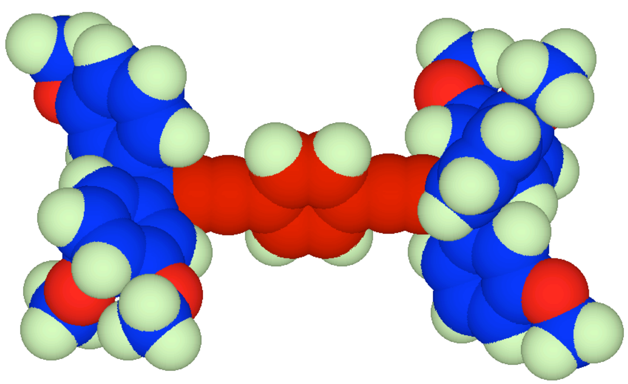
ORTEP:
Thermal Ellipsoids (ADP)

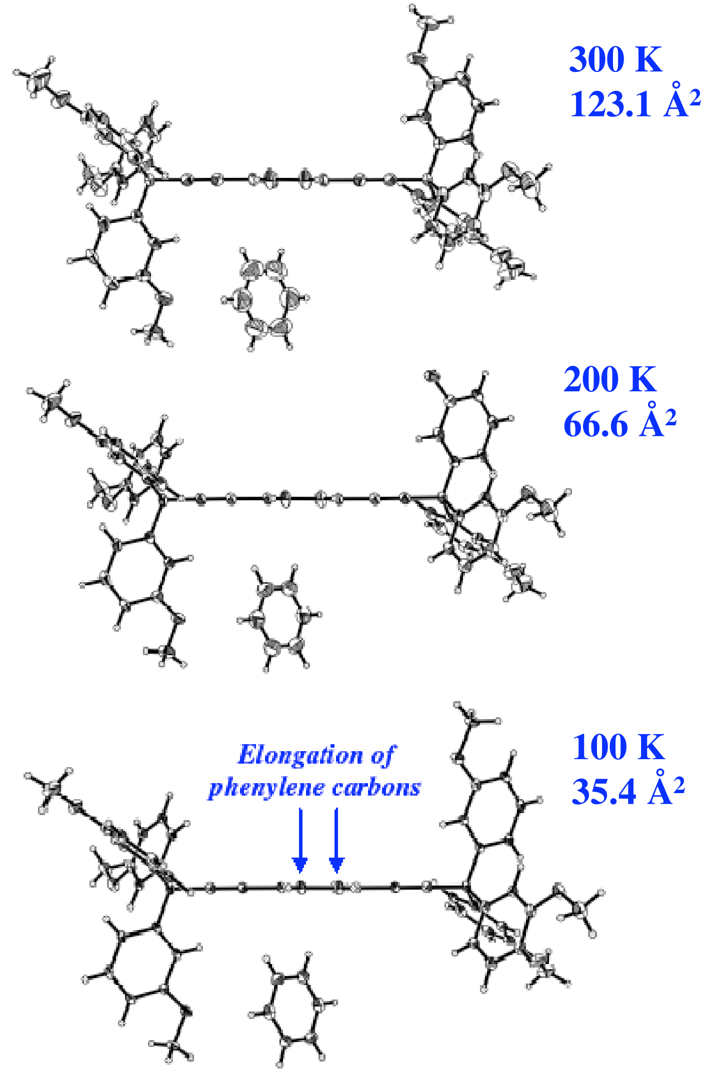
Rotational Dynamics by X-Ray Diffraction

Thermal Ellipsoids (ADP)

—V(x)= Ea (1-cos 2□)/2
For short displacements:
—Ea = 2RT / (4□ ²)



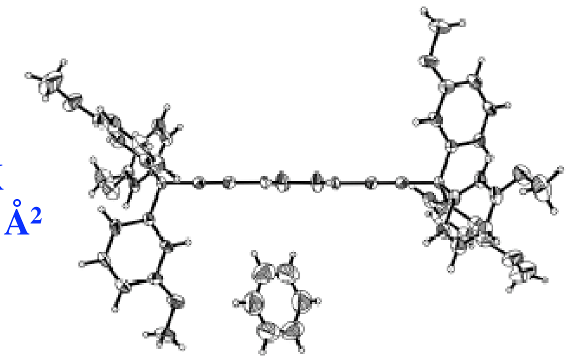




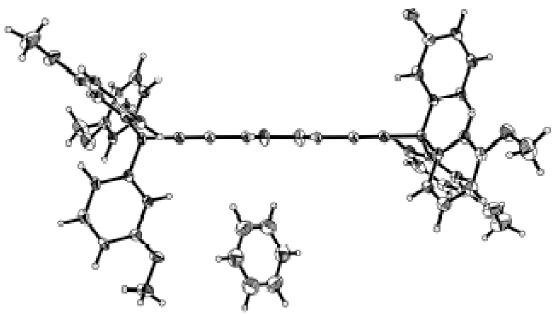
Ea = 9.8 kcal/mol

X-Ray Diffraction vs VT-NMR

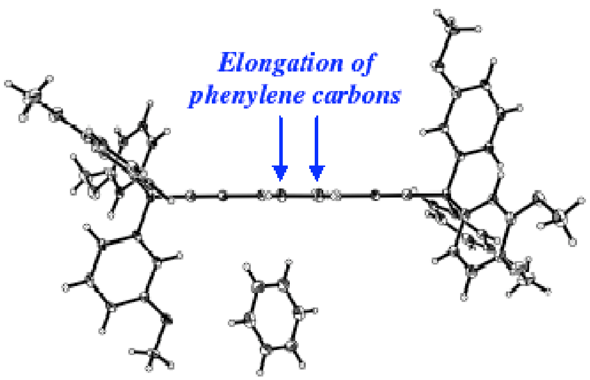
300 K
123.1 Å^2



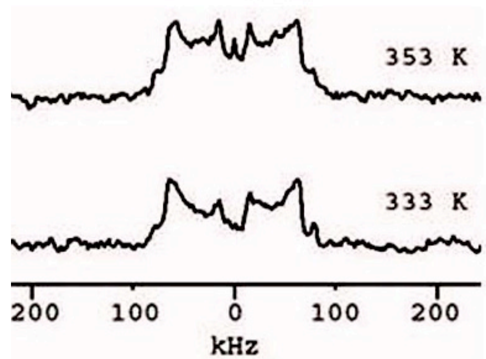
200 K
66.6 Å^2

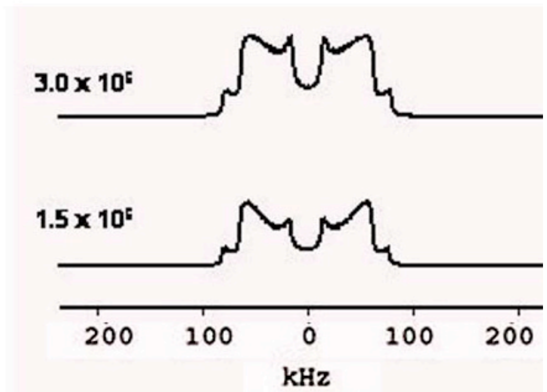


100 K
35.4 Å^2

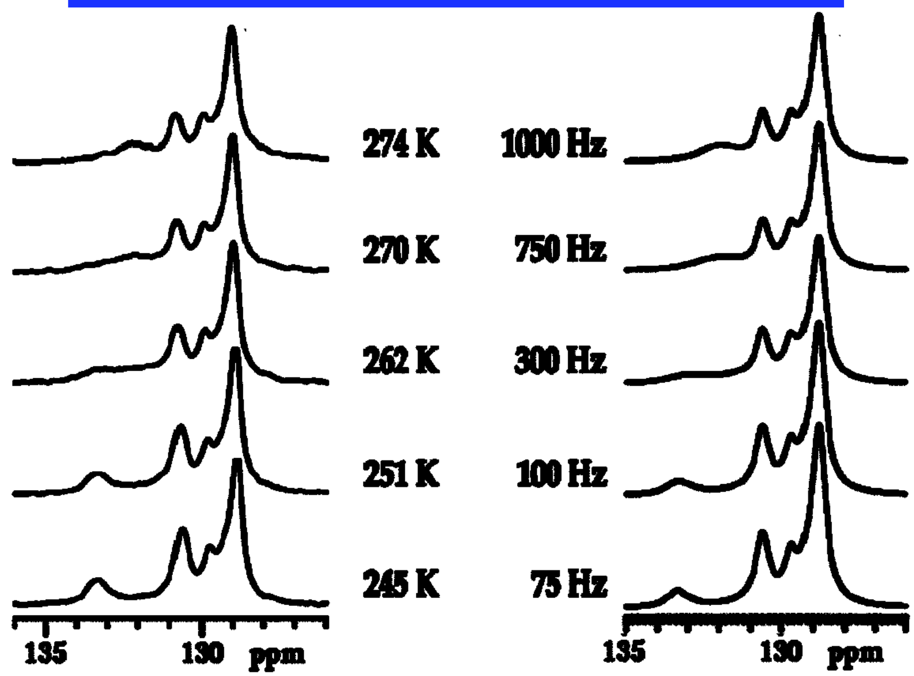


Ea = 9.8 kcal/mol





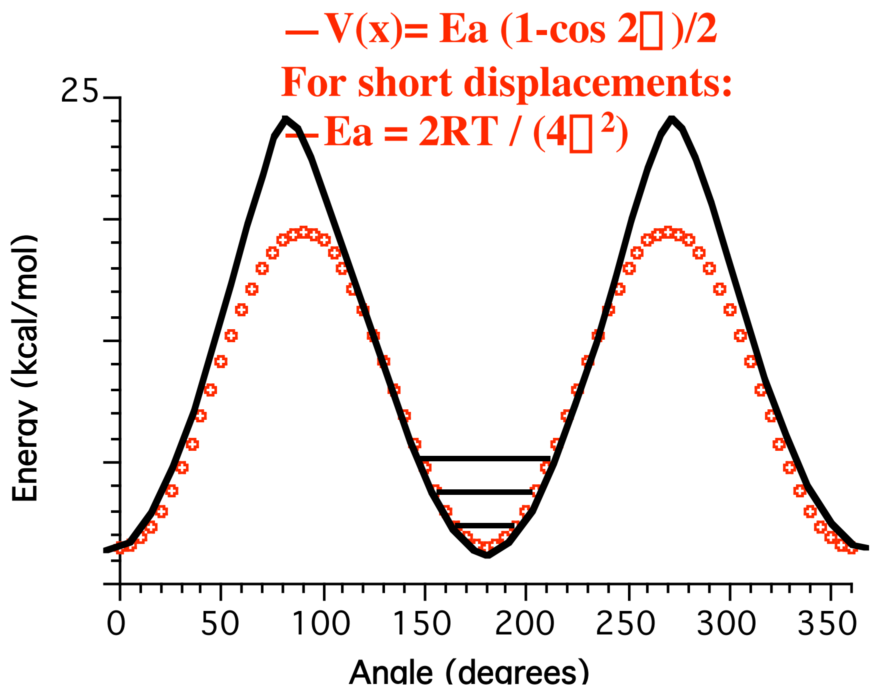
Ea= 11.5 kcal/mol; A=3x10^{13} s^{-1}

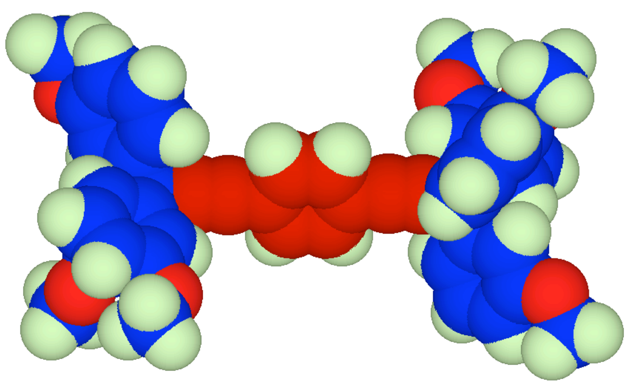


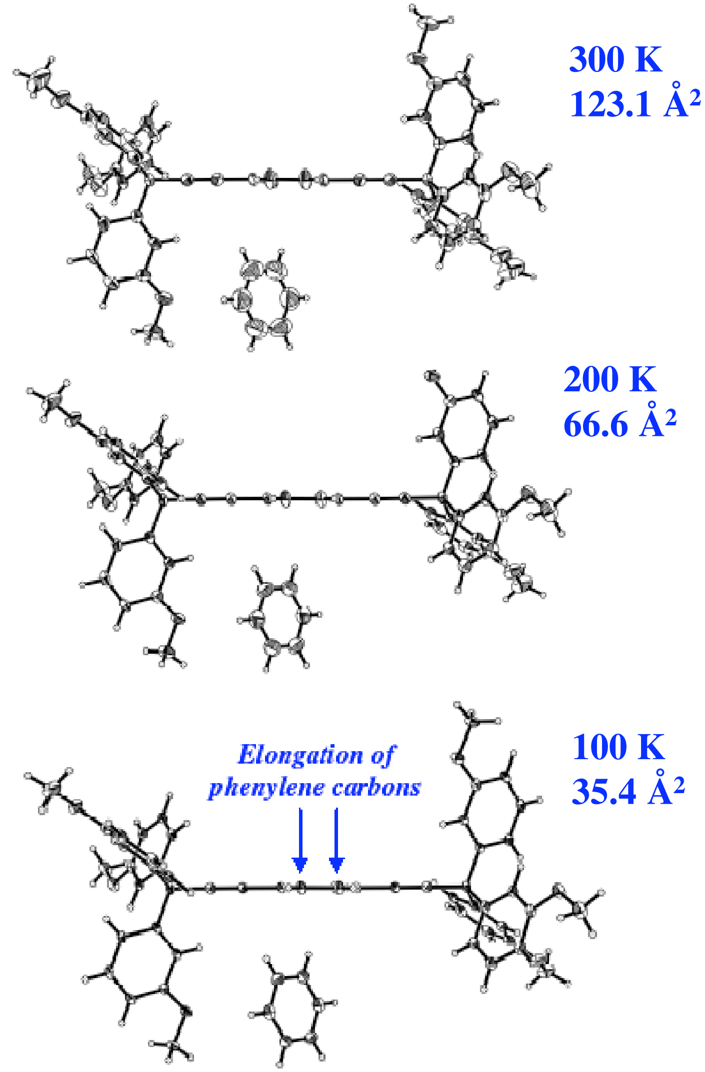
Ea =11.7 kcal/mol; A = 1.7x10^{12} s^{-1}.

Rotational Dynamics by X-Ray Diffraction

Thermal Ellipsoids (ADP)

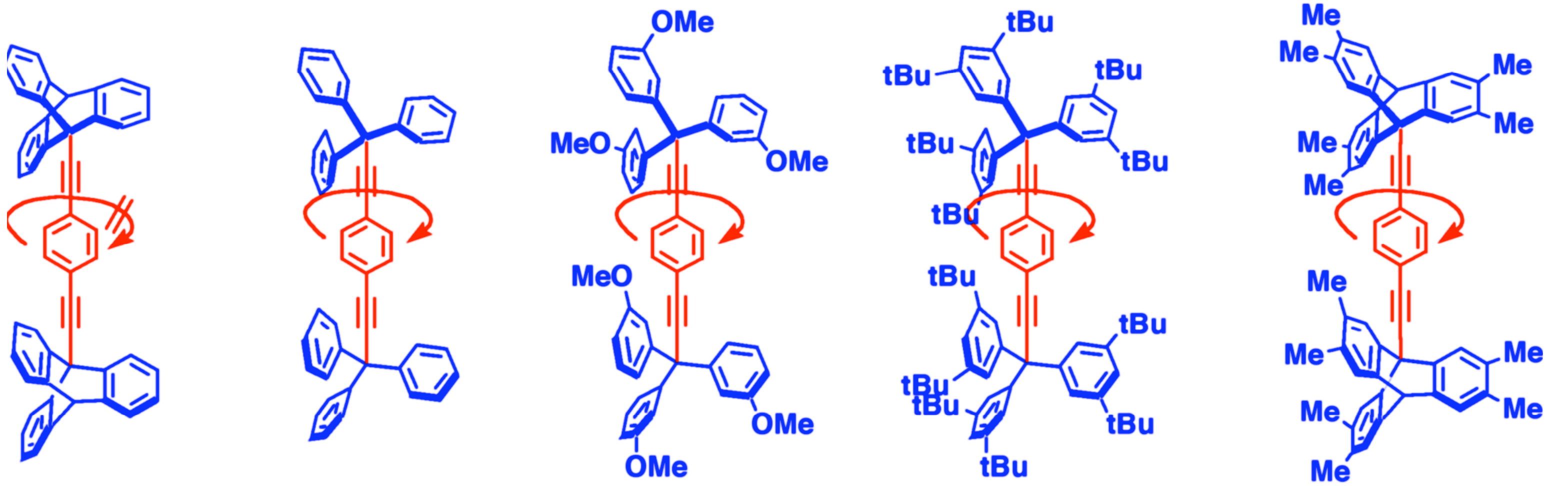






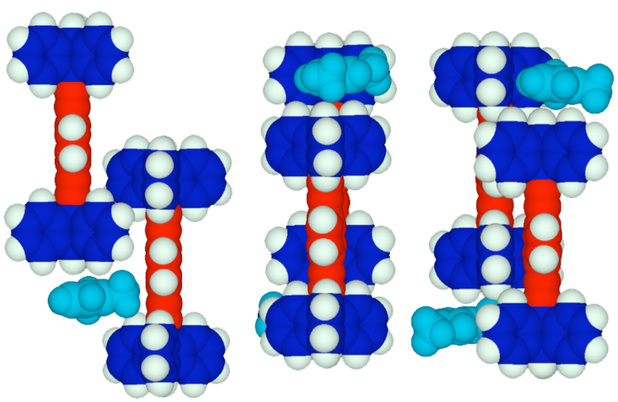
Ea = 9.8 kcal/mol

Stator Effects on Rotary Motion (ca. 0-10^{10} s^{-1})

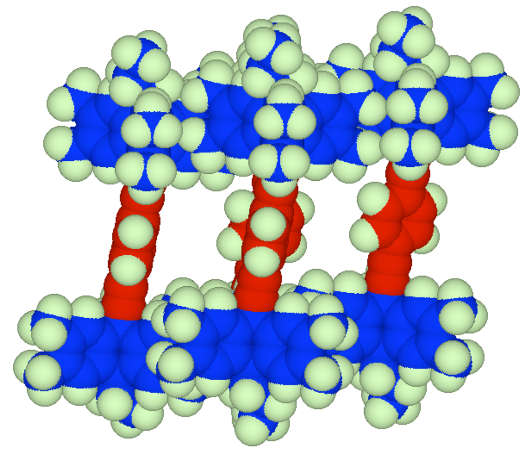


1	2	3	4	5
static	***1.3 MHz (at 65 °C)***	***1.5 MHz (at 60 °C)***	***> 100 MHz (at 20 °C)***	***6.5 MHz (-100 °C)***

1



5

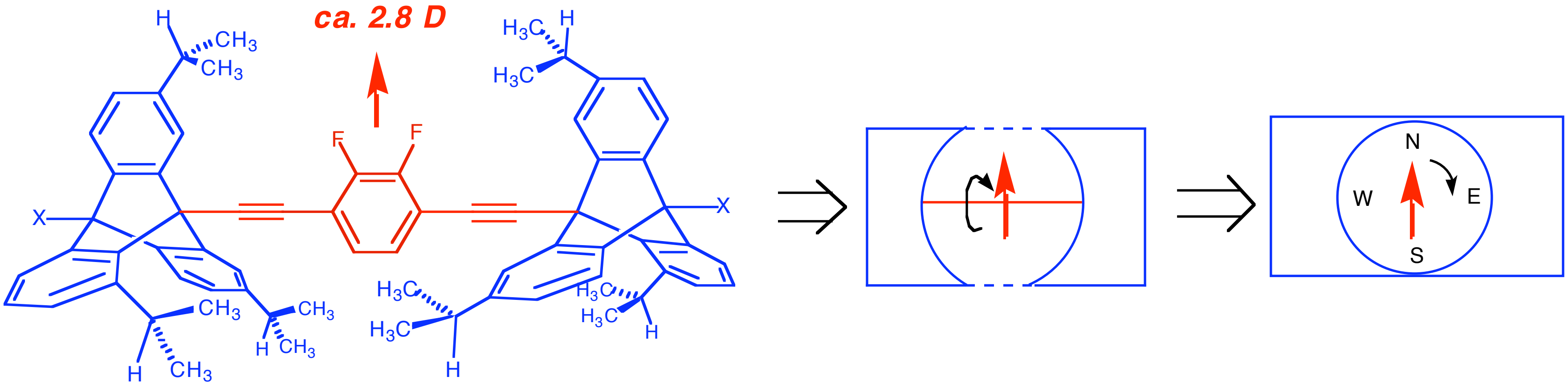


Godinez, et al., *JACS*. **2002**, *124*, 4701-4707.

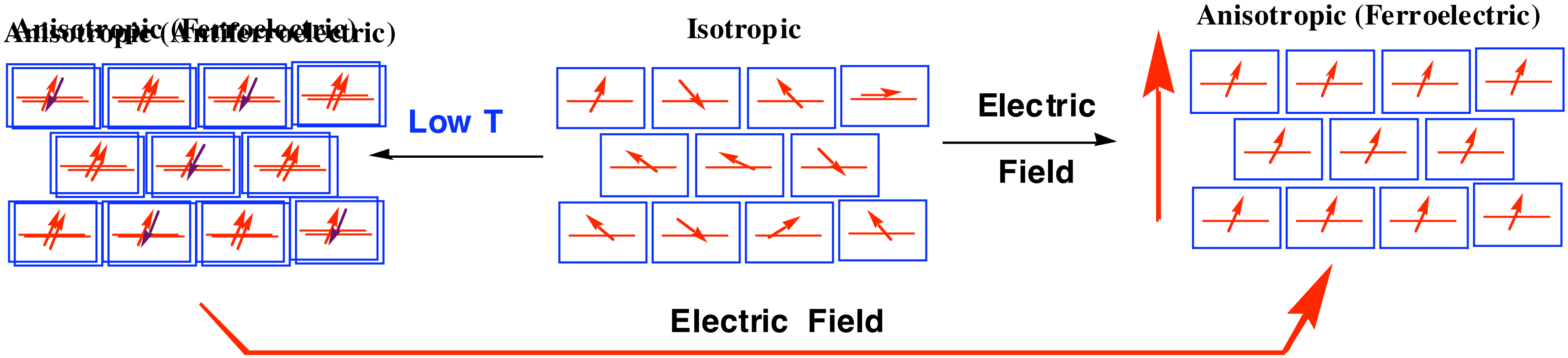
Godinez, et al., *JOC*. **2004**, *69*, 1652.

Feature article: Garcia-Garibay,M. *Proc. Natl. Acad. Sci, USA,* ***2005****, 102*, 10771-10776 .

Molecular Compasses



Photonic Materials

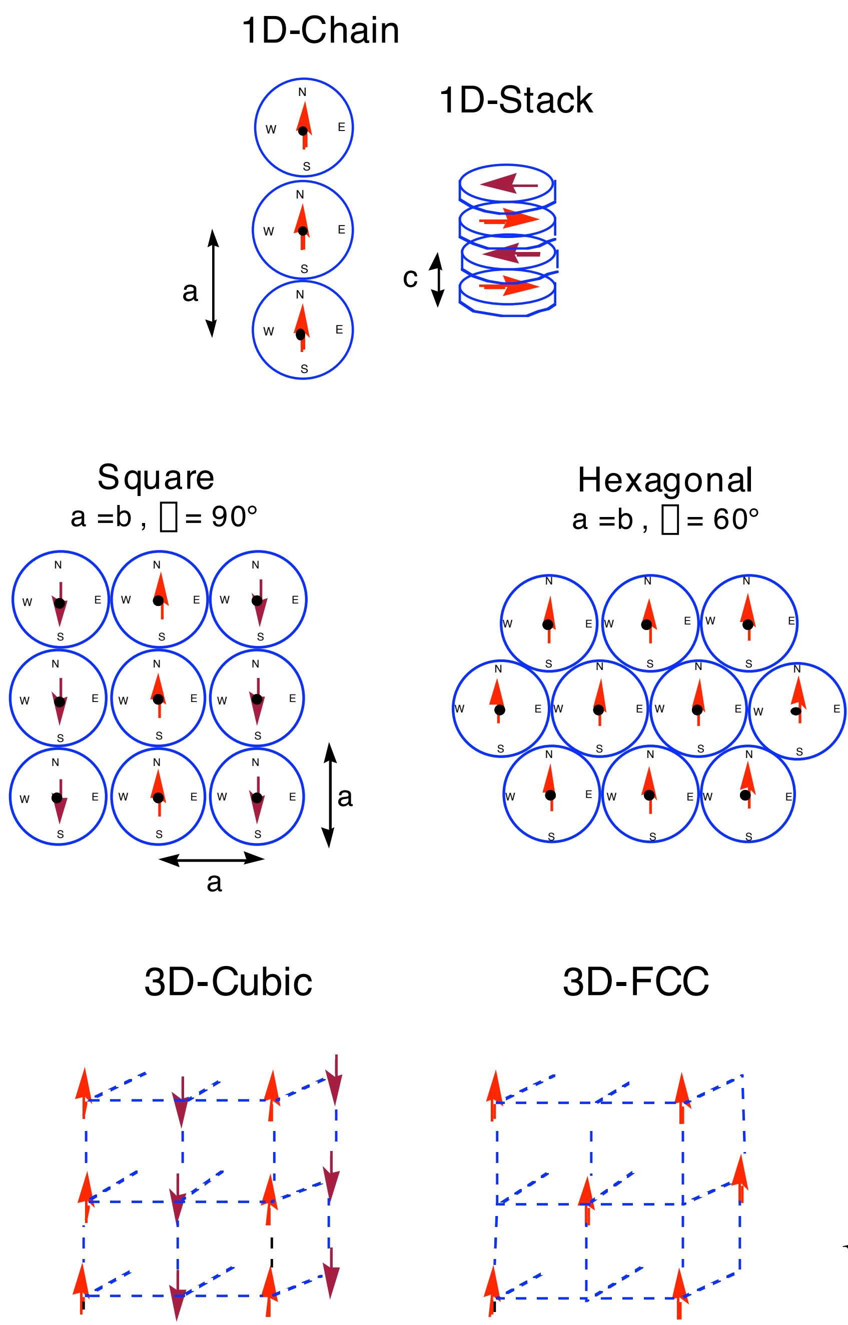


-Dichroism
-Birefringence
-NLO

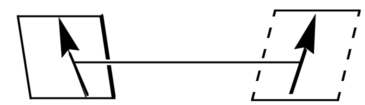
<u>Electric Dipoles</u>

Frictionless => Switches
Hindered => Polar Materials, Electrets

Reorienting Dipole Lattices



E_{dd} = □$_i$□$_j$ / □(r_{ij})^3 [cos□-3cos□$_1$cos□$_2$)



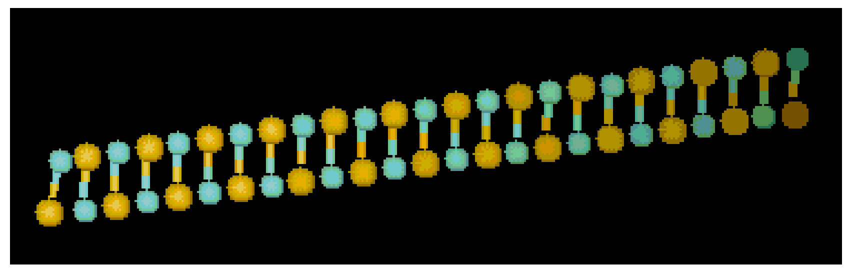
□=dielectric constant

□=dihedral angle between dipoles

□$_1$, □$_2$ =angle between dipole vector and line

R_{ij} = distance between dipoles

M. Ratner



$$f_0 = \frac{1}{2\square}\sqrt{\frac{k_B T_0}{I}} \;\square\; 100 \text{ GHz}$$

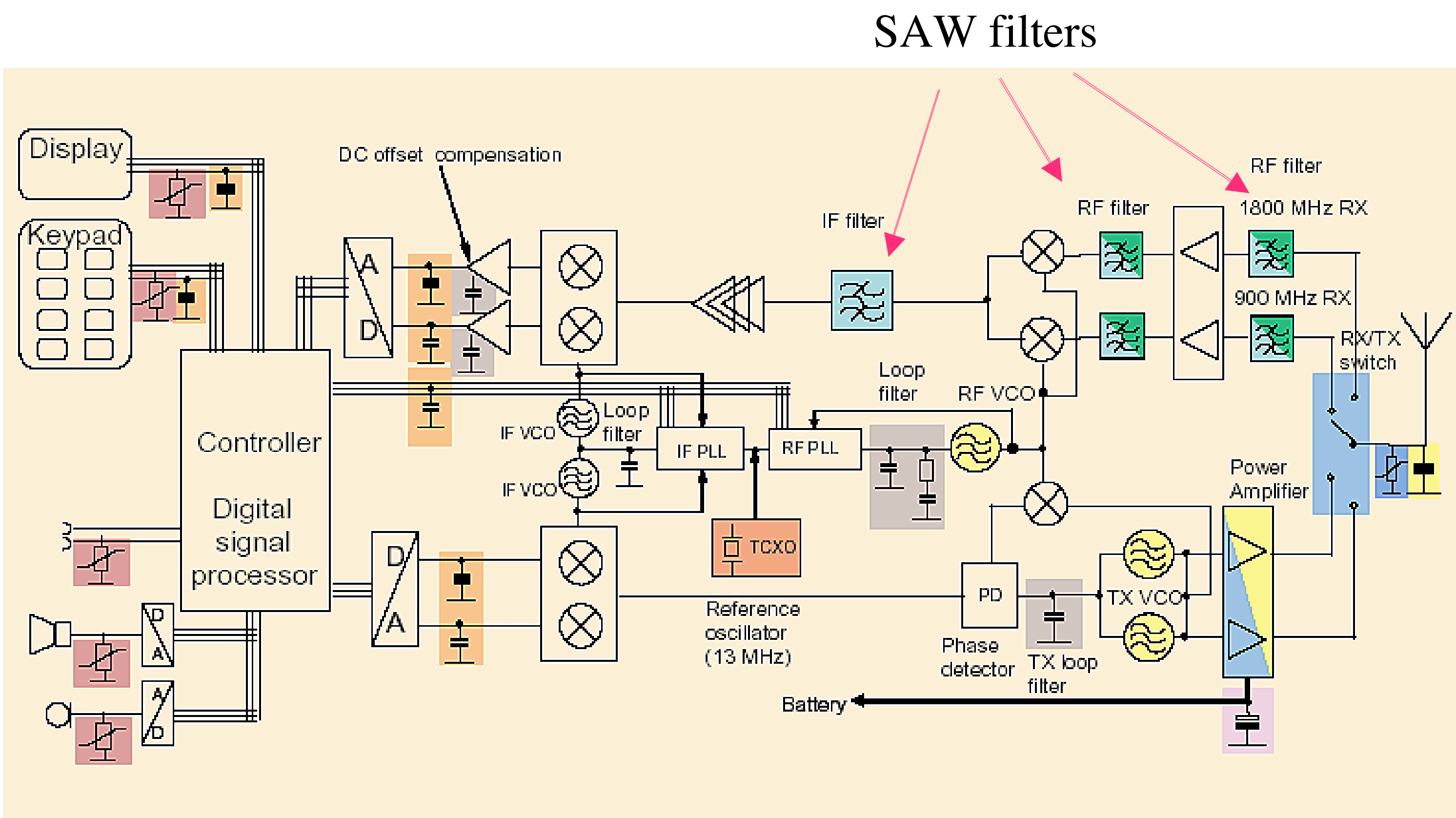
interaction energy

moment of inertia

$$v_R \;\square\; f_0 a \;\square\; 100 \text{ GHz} \cdot 10 \text{ Å} = 100 \text{ m/s}$$

lattice constant

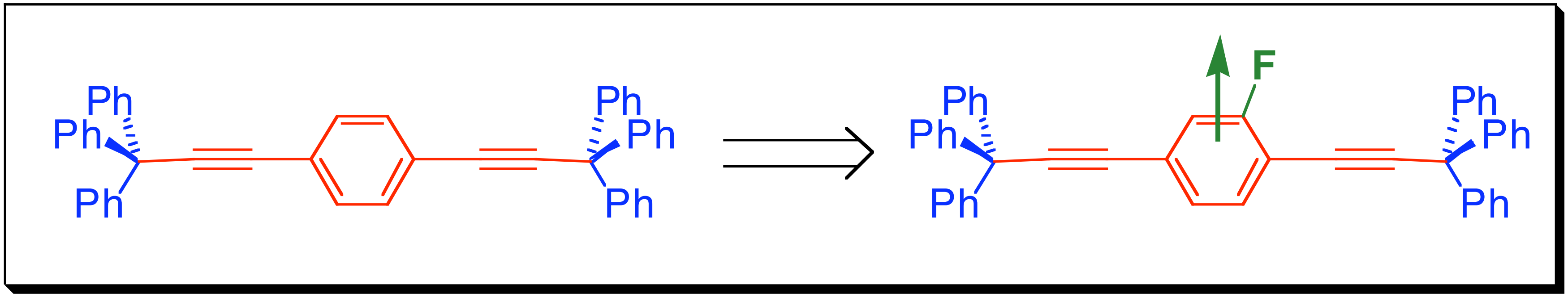
Surface Acoustic Wave Filters and Delay Lines

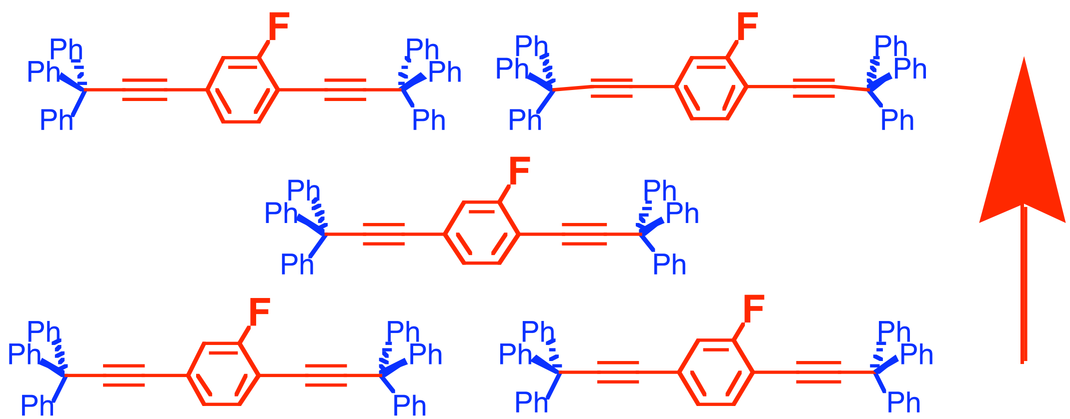


Schematic of a GMS cell phone handset (EPCOS)

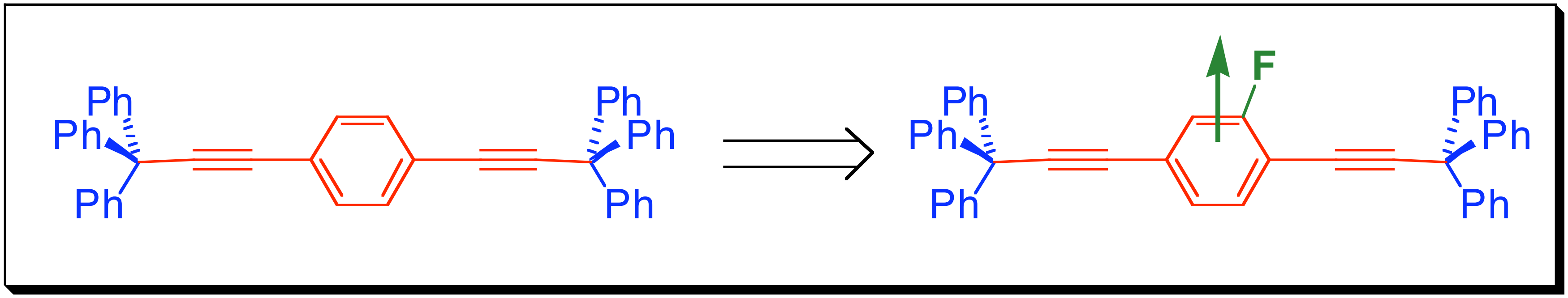
More than 1 billion SAW devices are sold annually

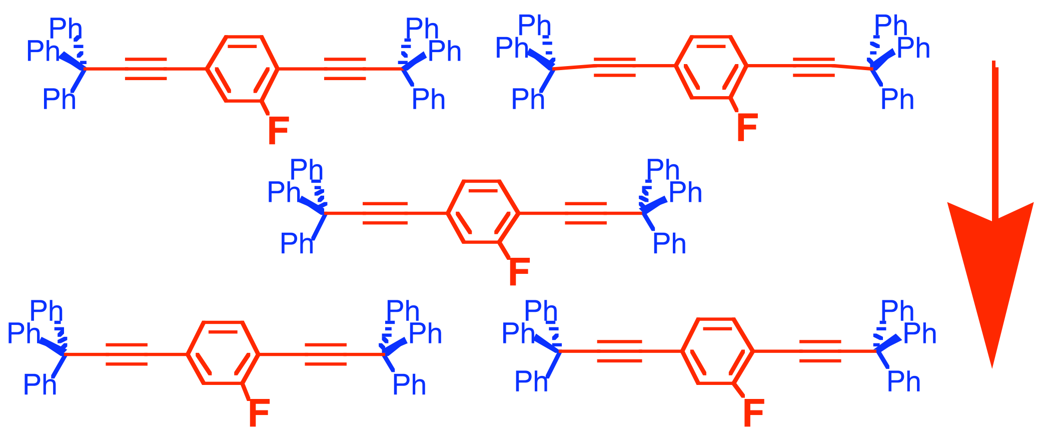
Rotational Dynamics: Two-fold flip



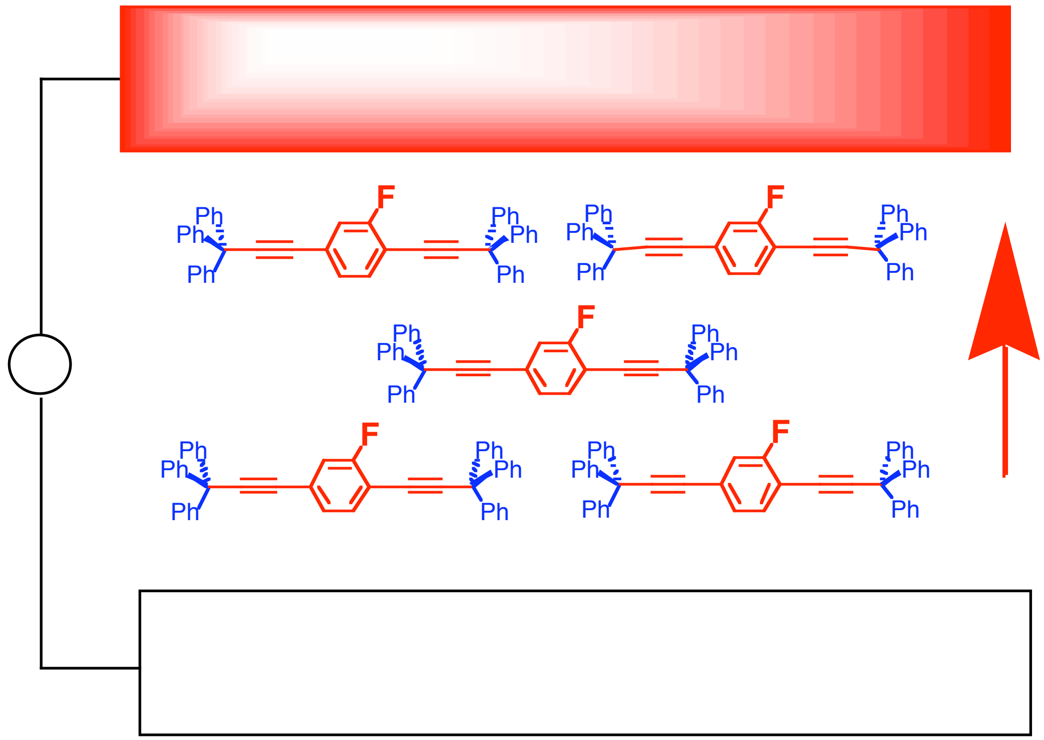


Rotational Dynamics: Two-fold flip



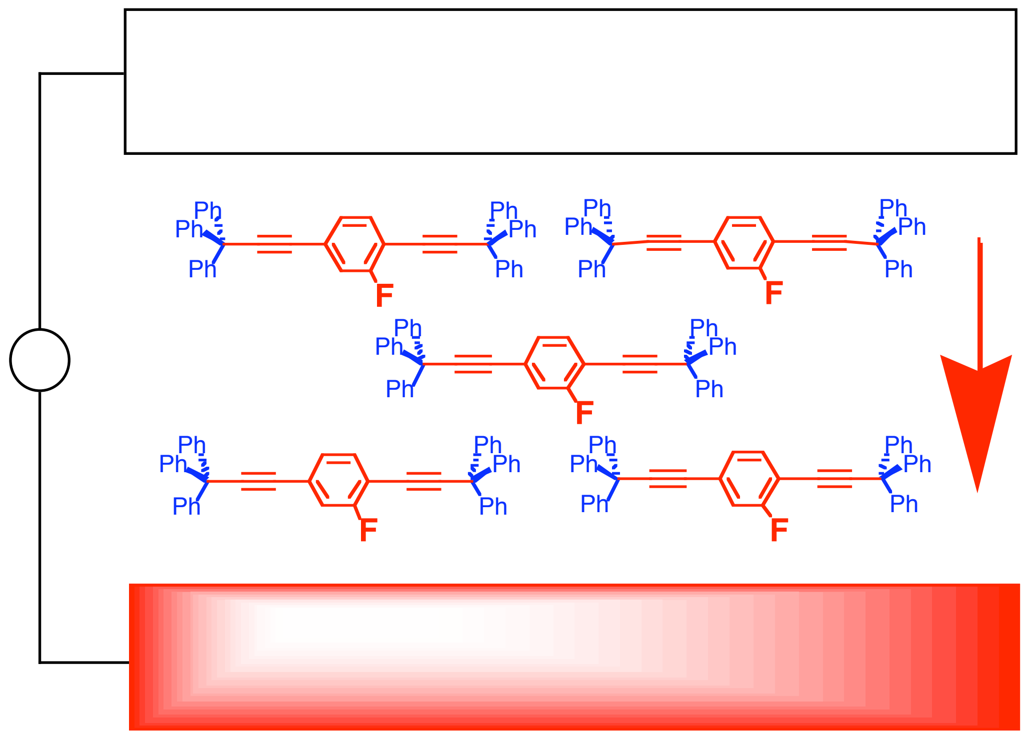


Dielectric Measurements



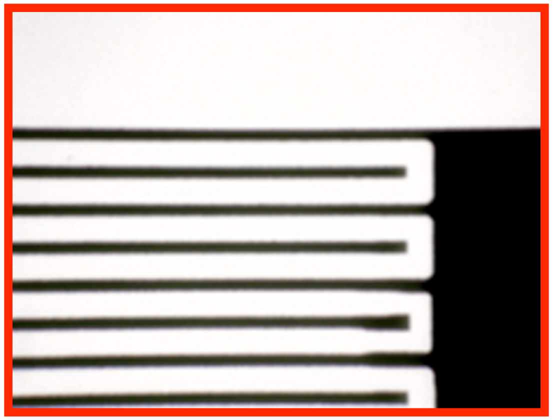
(Electric Energy is Absorbed when AC Frequency Matches that of the Internal Dipole Dynamics)

Dielectric Measurements

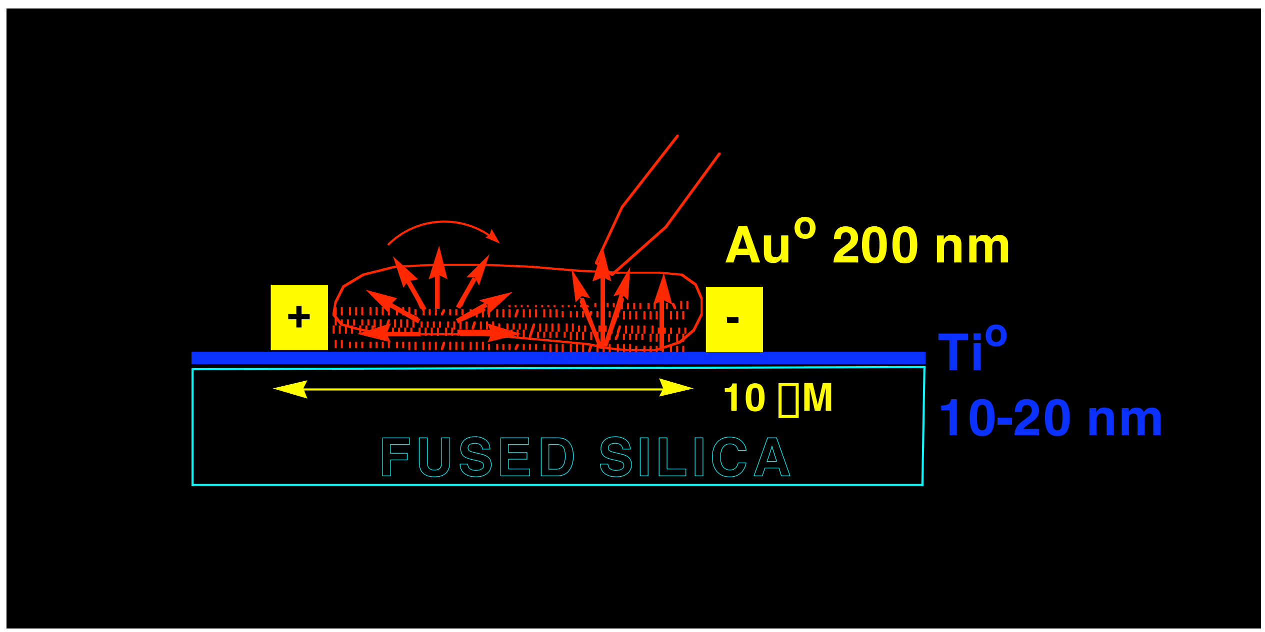


(Electric Energy is Absorbed when AC Frequency Matches that of the Internal Dipole Dynamics)

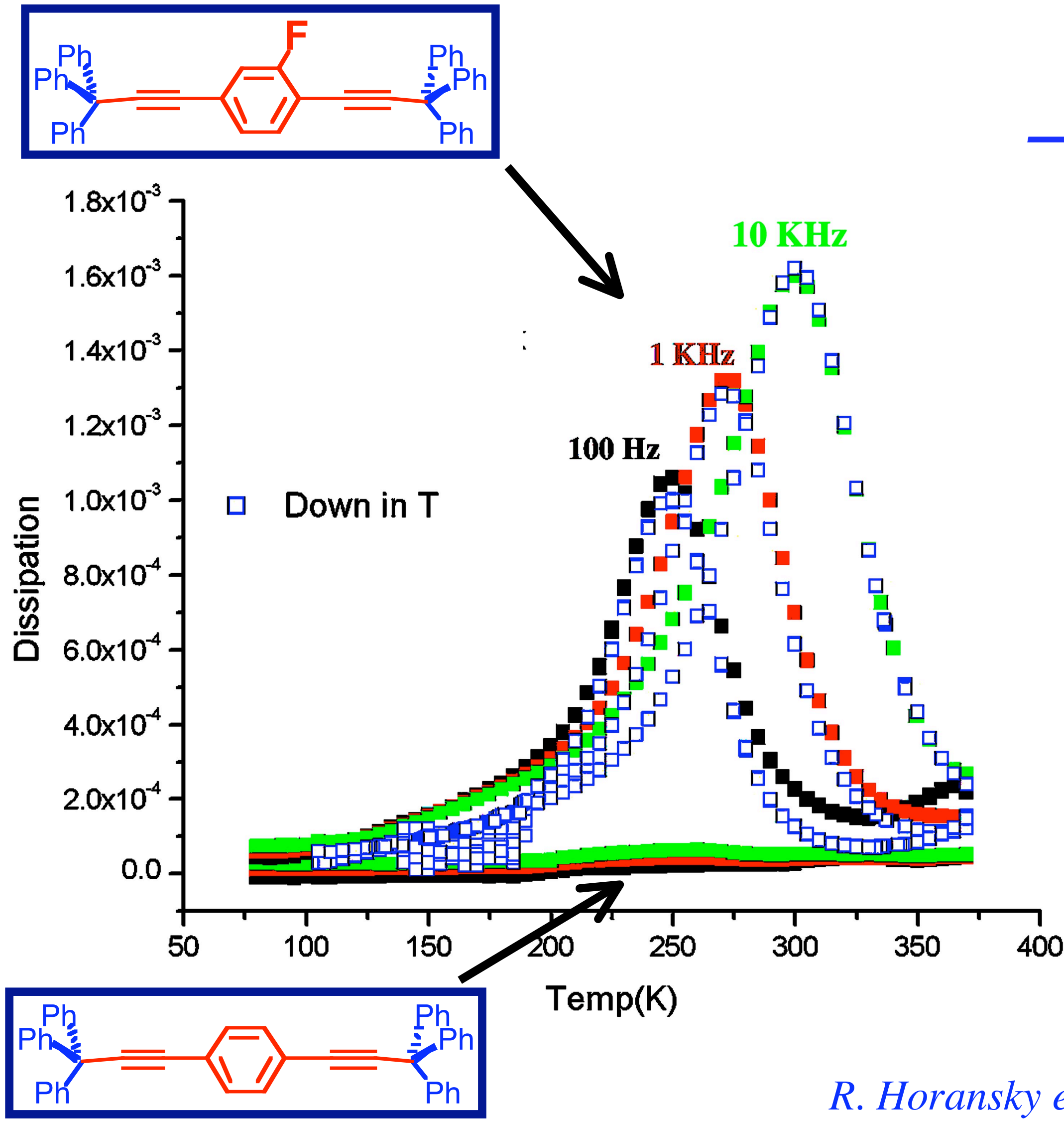
Dielectric Measurements



Interdigitated Electrodes Patterned Photolithographically by Wet Etching



F-Rotor: Frequency-Dependent Dielectric Measurements



—Polycrystalline samples

a) Non-Polar Rotor Gives Baseline

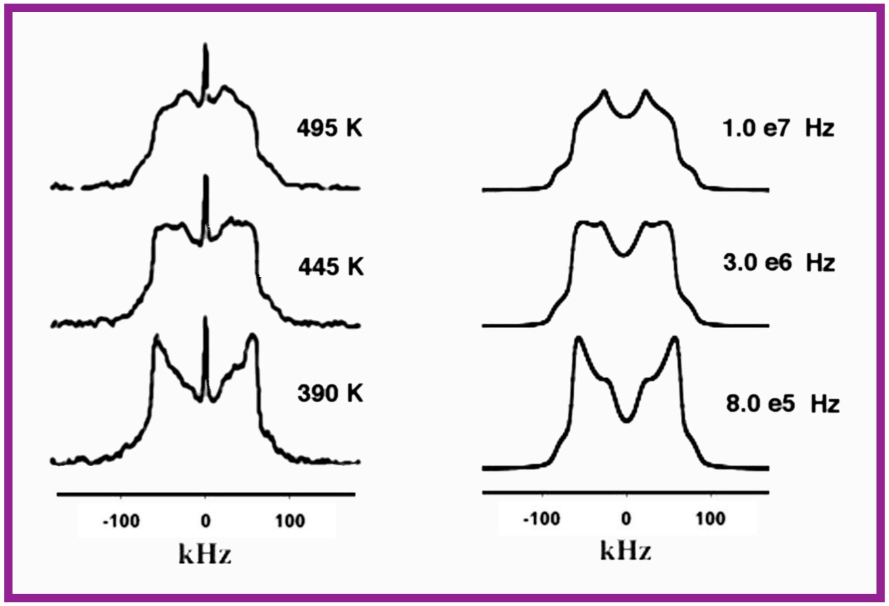
b) Reversible on Heating and cooling cycles

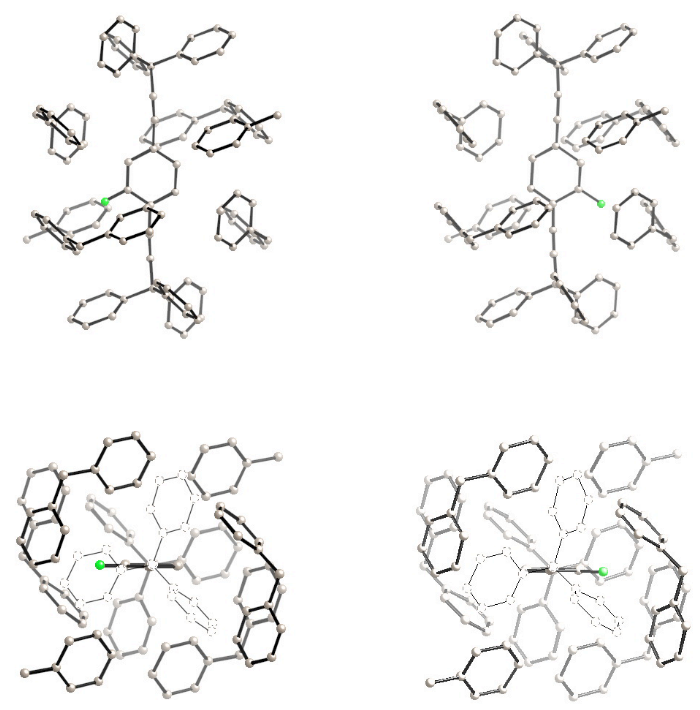
c) Peak Position Depends on AC Freq.

d) Signal Intensity Increases With Temp.

R. Horansky *et al. Phys. Rev. B.*, **2005**, 72_014302.

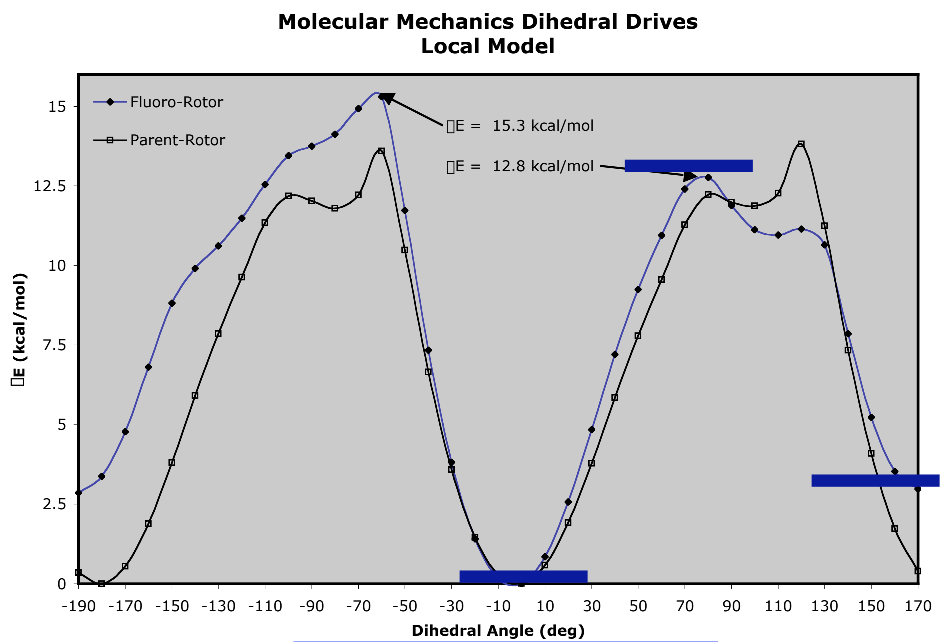
F-Rotor: Force-Field Estimate of Rotational Potential





Favored State (170°)

Disfavored State (0.0°)

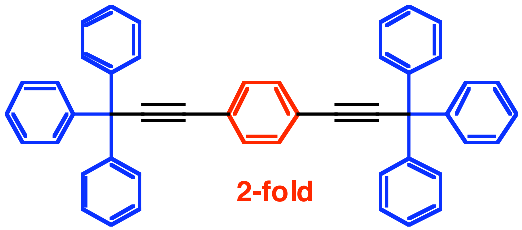


DIELECTRIC
Ea = 13.7 kcal / mol
ΔE = 1.4 kcal / mol

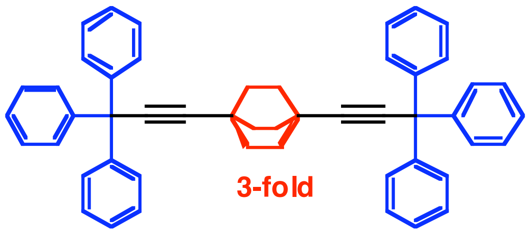
²H NMR
Ea = 12.4 kcal / mol
ΔE = 0.8 kcal / mol

Force-Field Potential
Ea=12.8 kcal/mol
ΔE= 2.5 kcal/mol

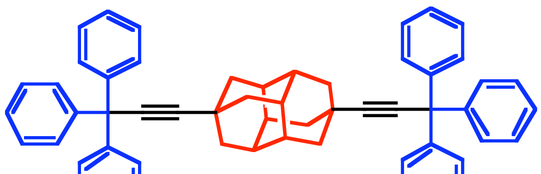
Rotator Effects on Rotary Motion ?



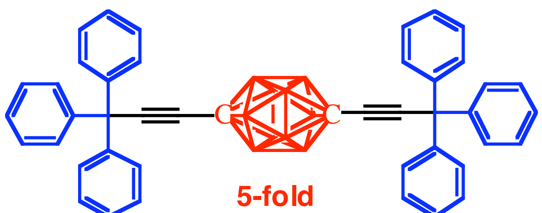
2-fold



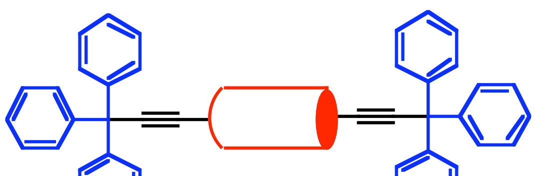
3-fold



3-fold
(6-fold)



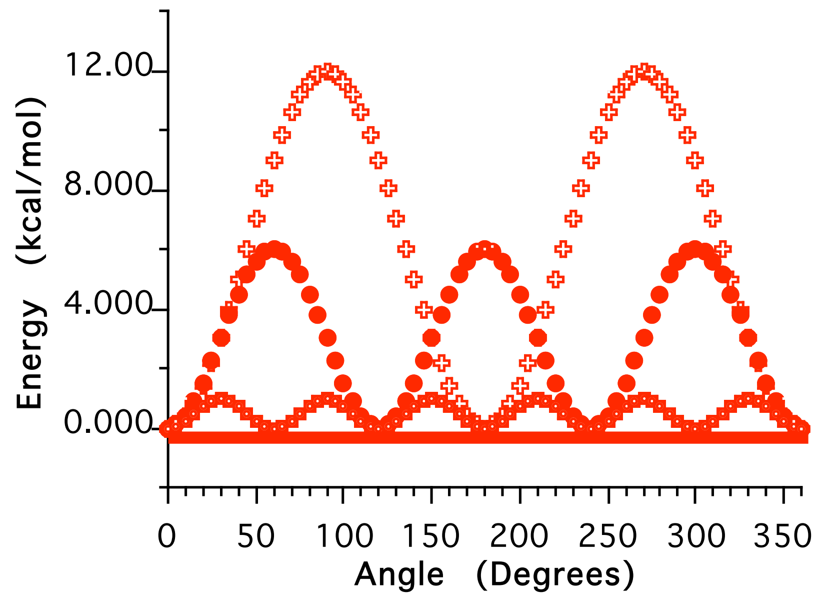
5-fold
(10-fold)

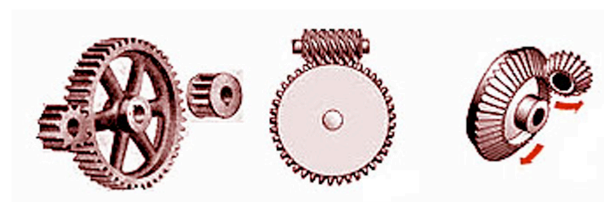


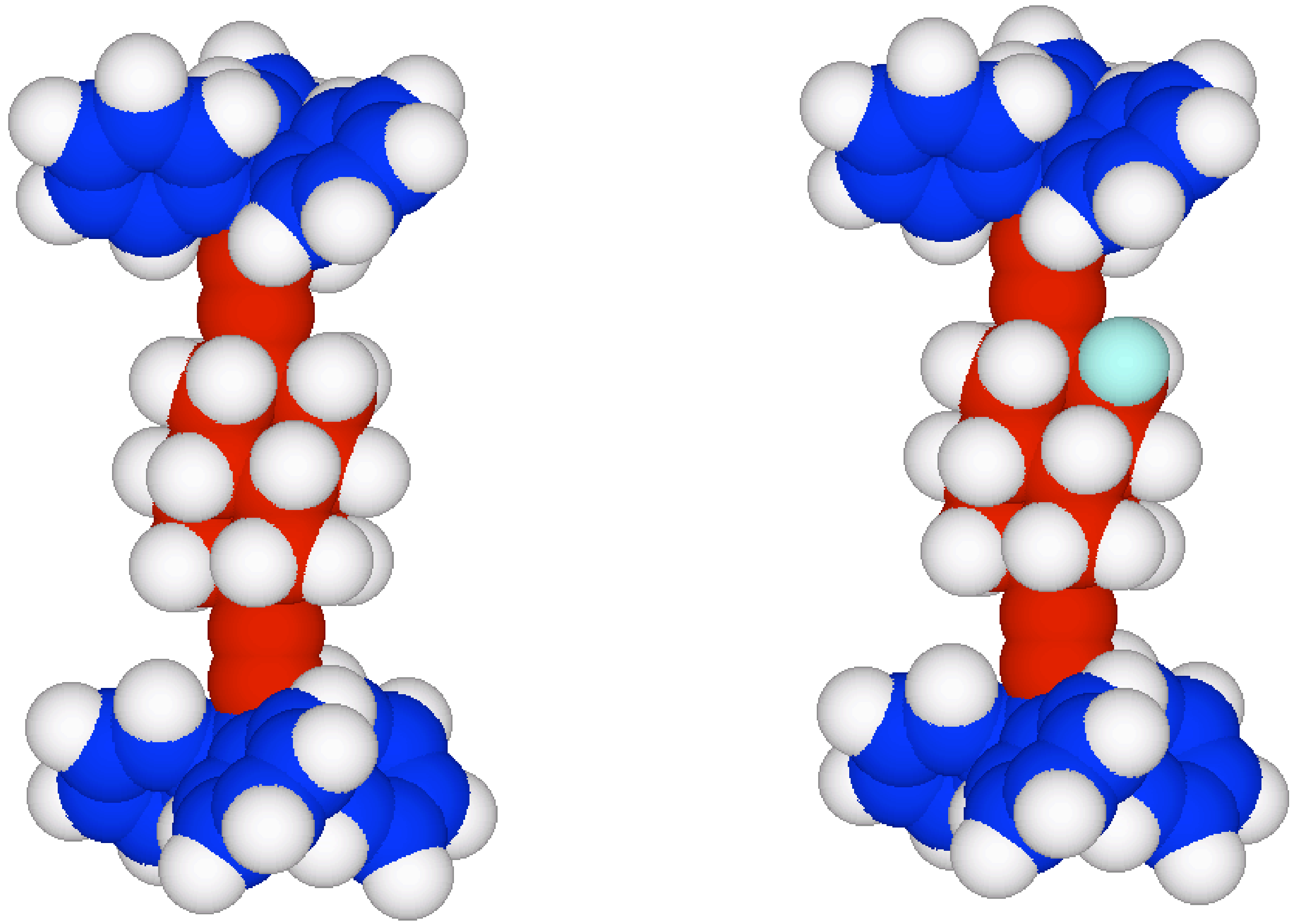
∞-fold

High Symmetry Order Rotors

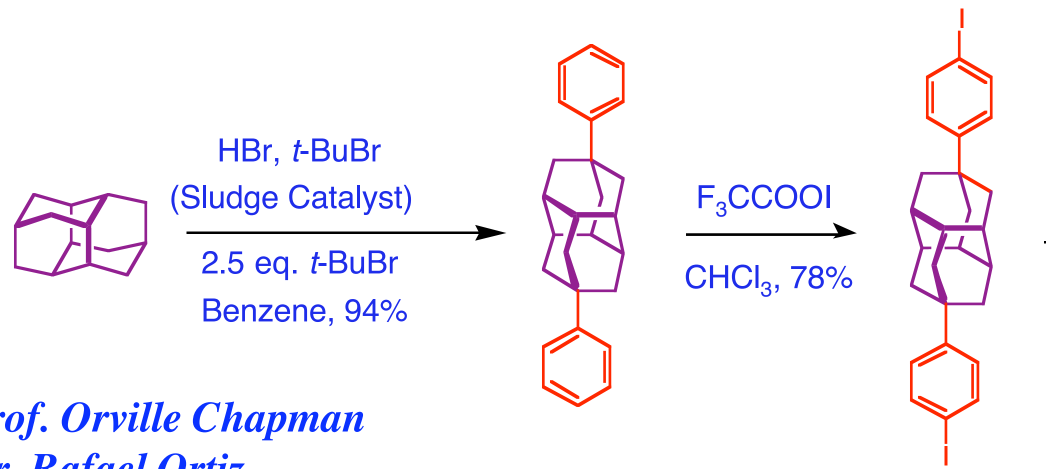
- *—Low rotational barriers*
- *—High radial resolution (polarity)*
- *—Cogitation (gearing)*





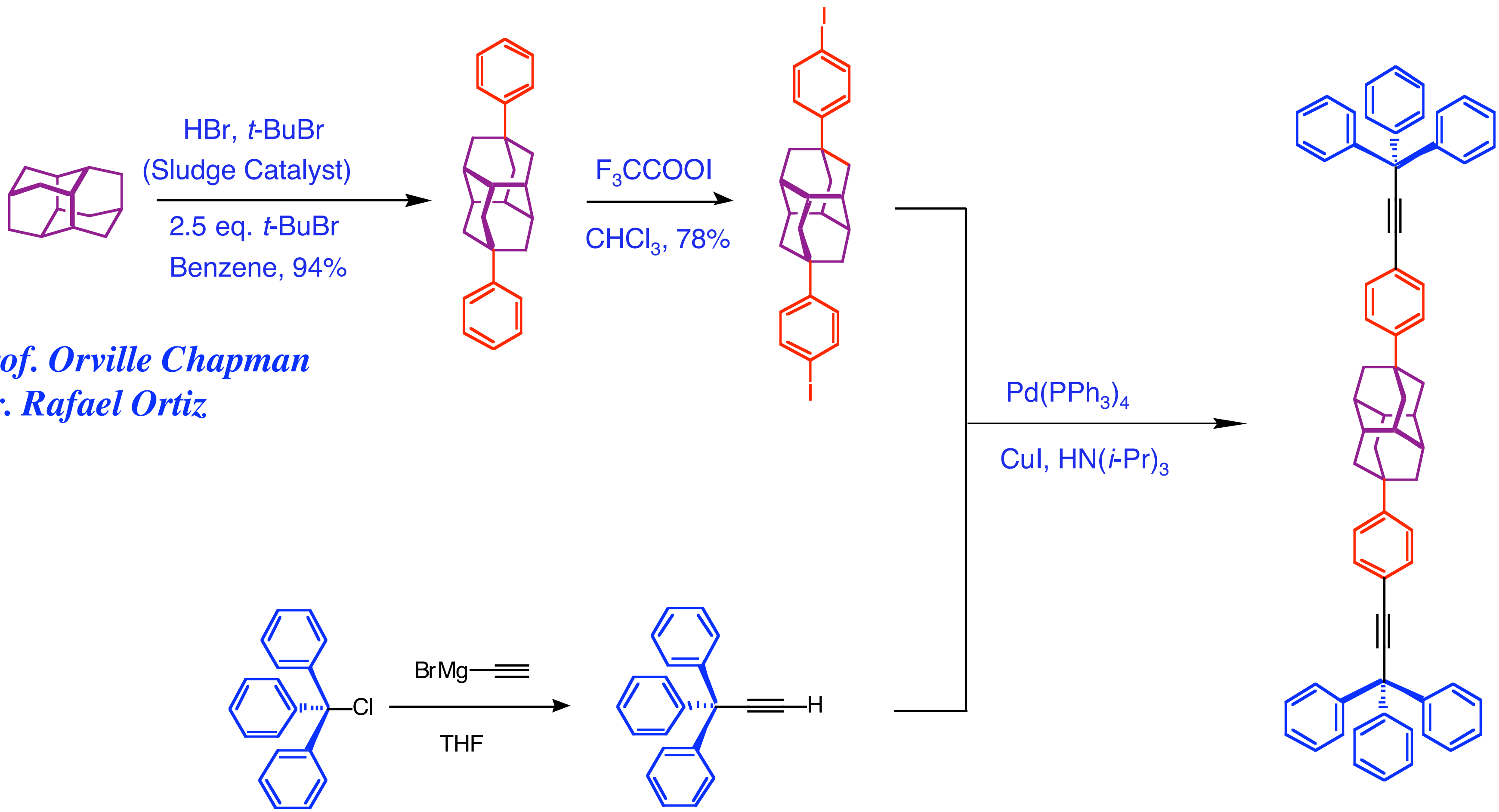


The right place, the right time….



Prof. Orville Chapman
Dr. Rafael Ortiz

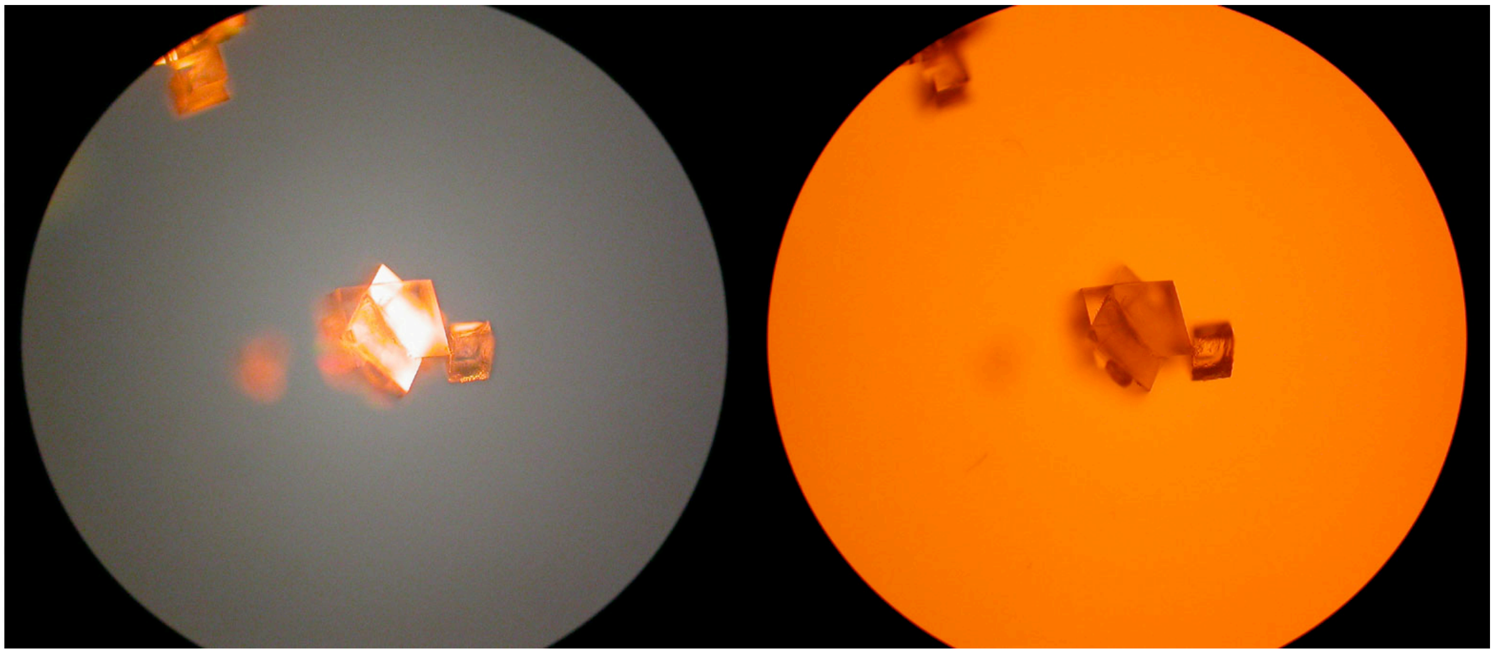
The right place, the right time….

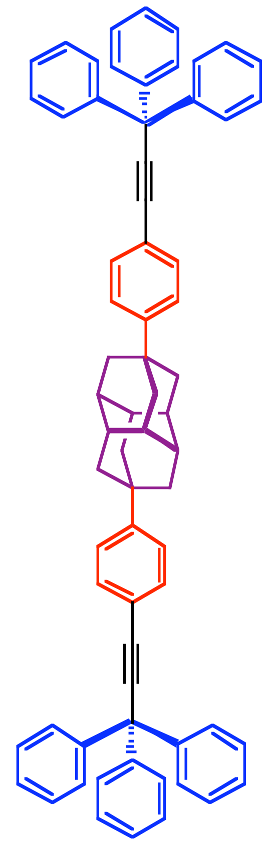


Prof. Orville Chapman
Dr. Rafael Ortiz

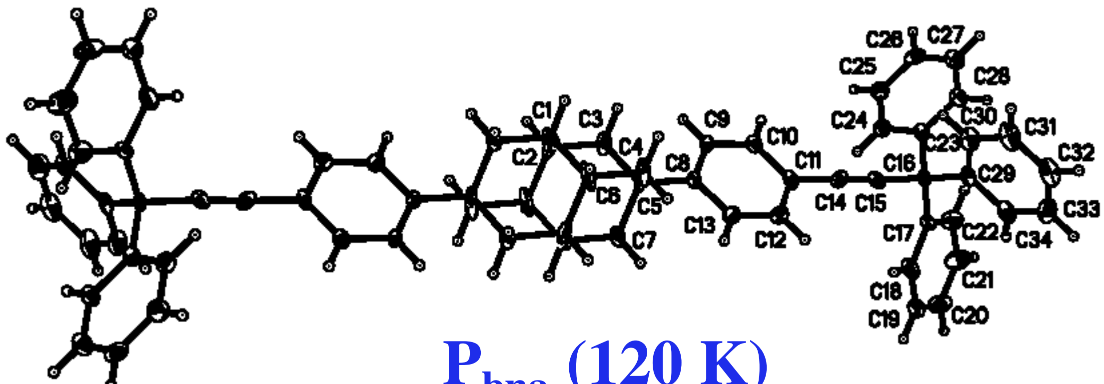
—Compare Rotatory Dynamics of Phenylene and Diamantene!

Bis(phenylene)diamantane Rotator system: X-Ray structure

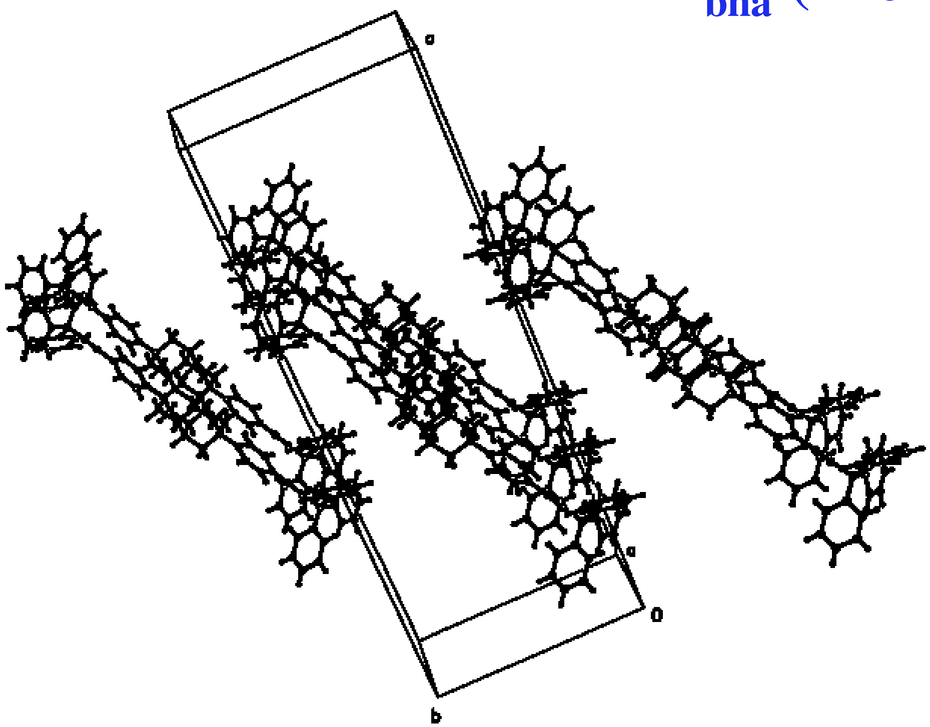




Bis(phenylene)diamantane Rotator system: X-Ray structure

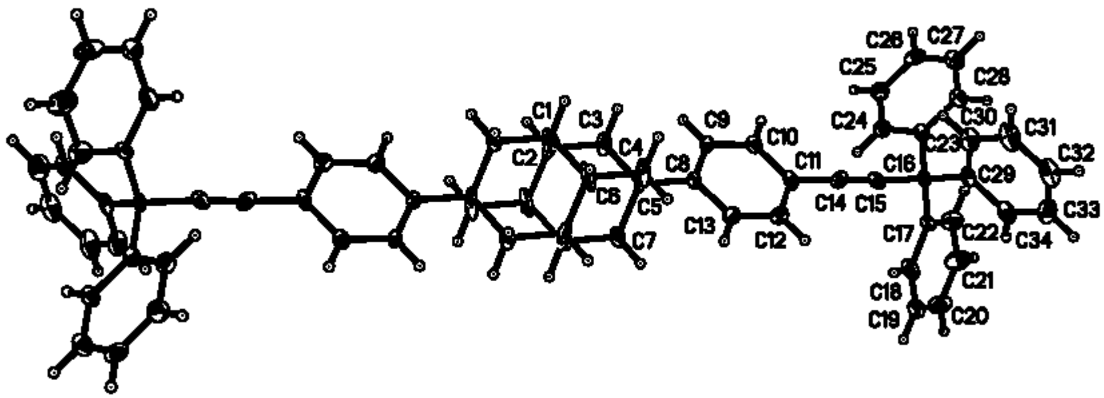


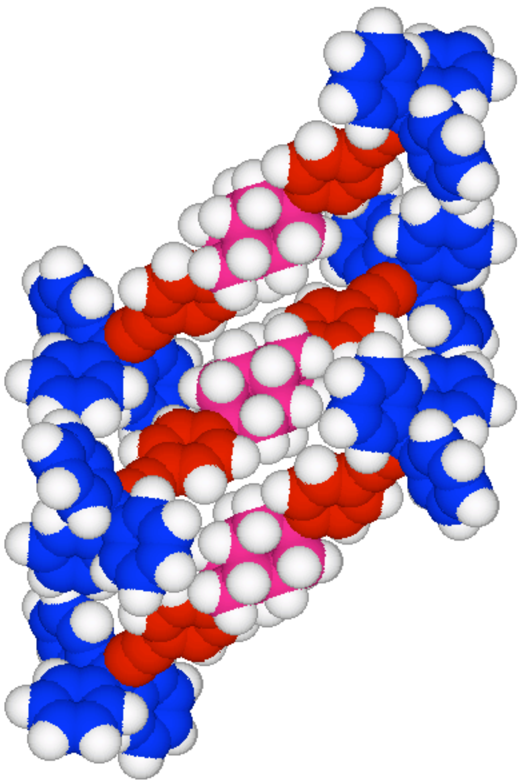
P_{bna} (120 K)



Log-stack packing

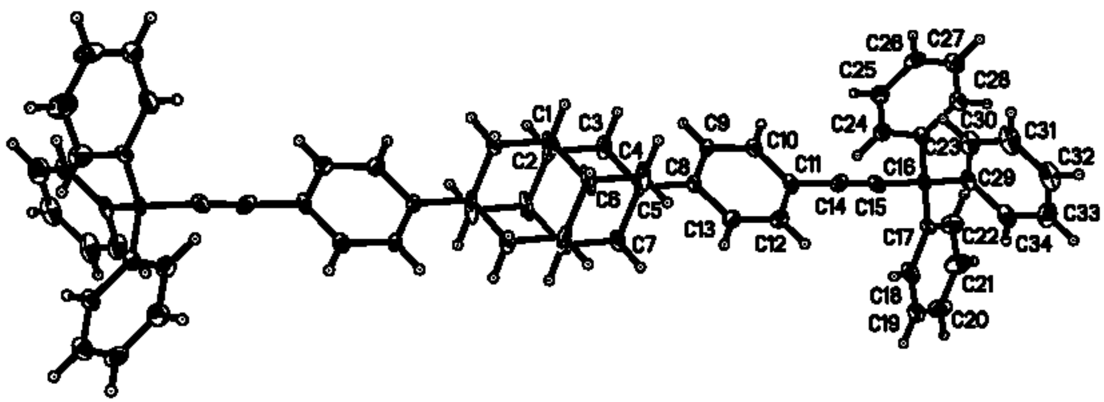
Diamantane Rotor



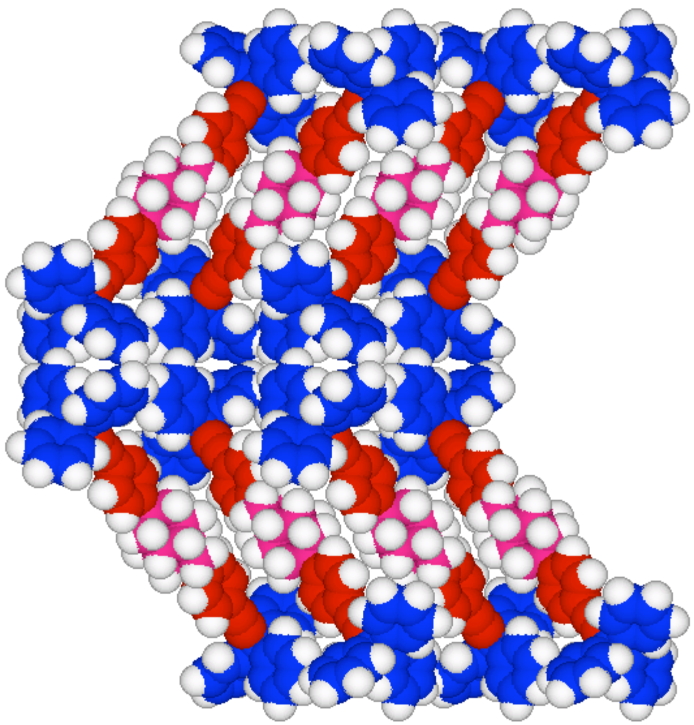


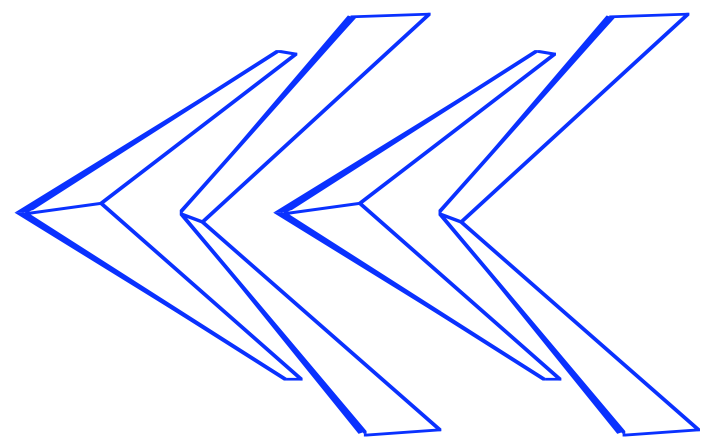
Log-stack packing

Diadamantane Rotor



four-fold phenyl embrace

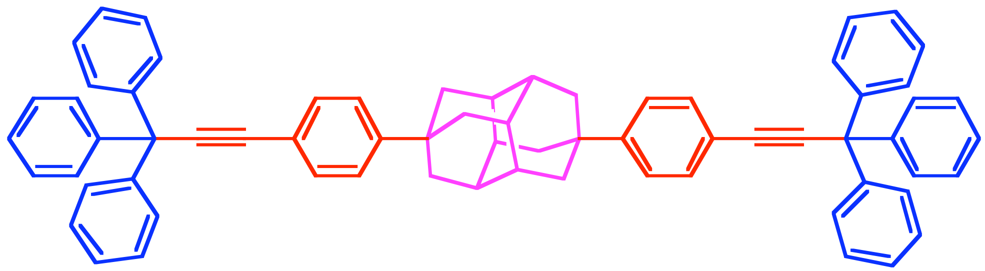


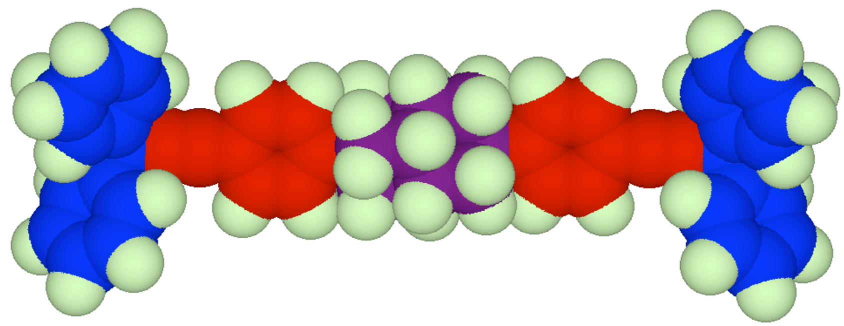


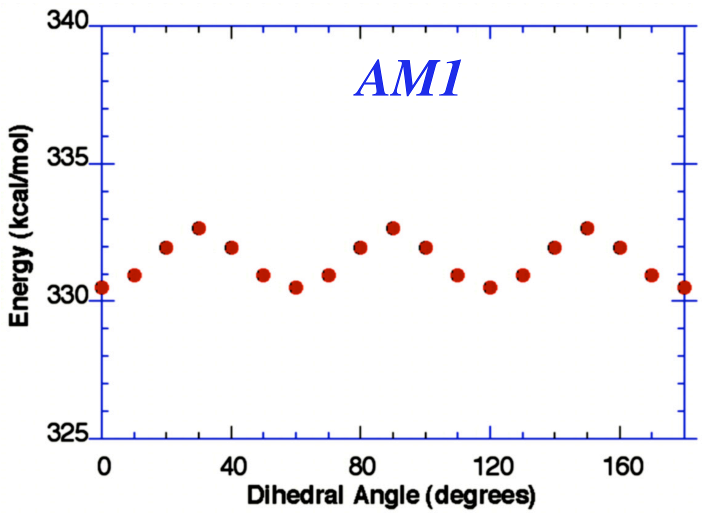
In-and-out Chevrons

Bis(phenylene)diamantane Rotator system:

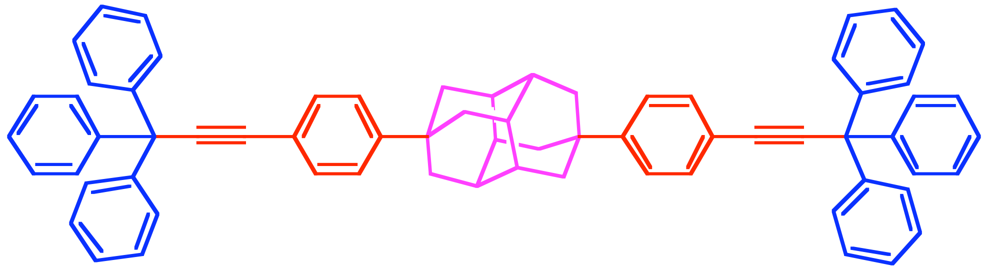
Intrinsic bis(phenylene)-diamantene rotational barrier



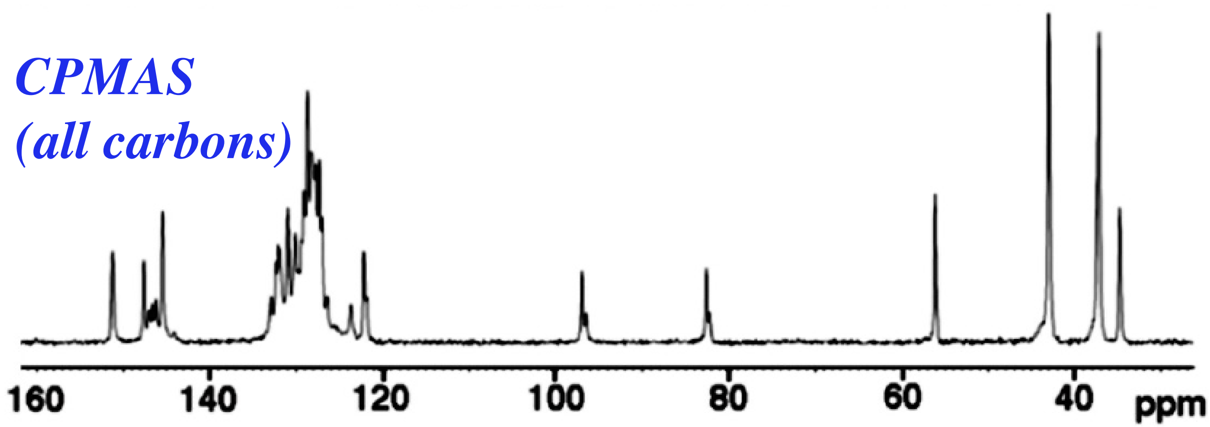


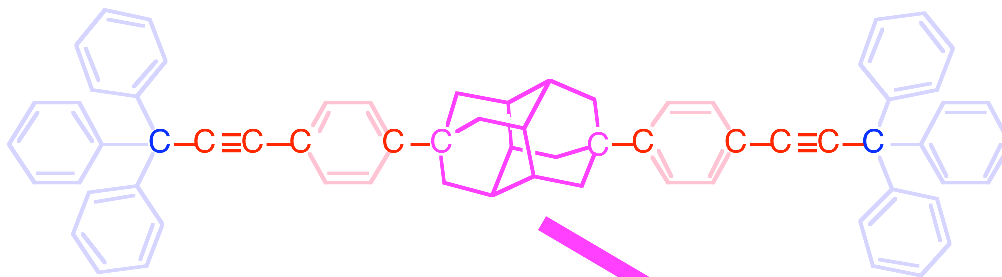


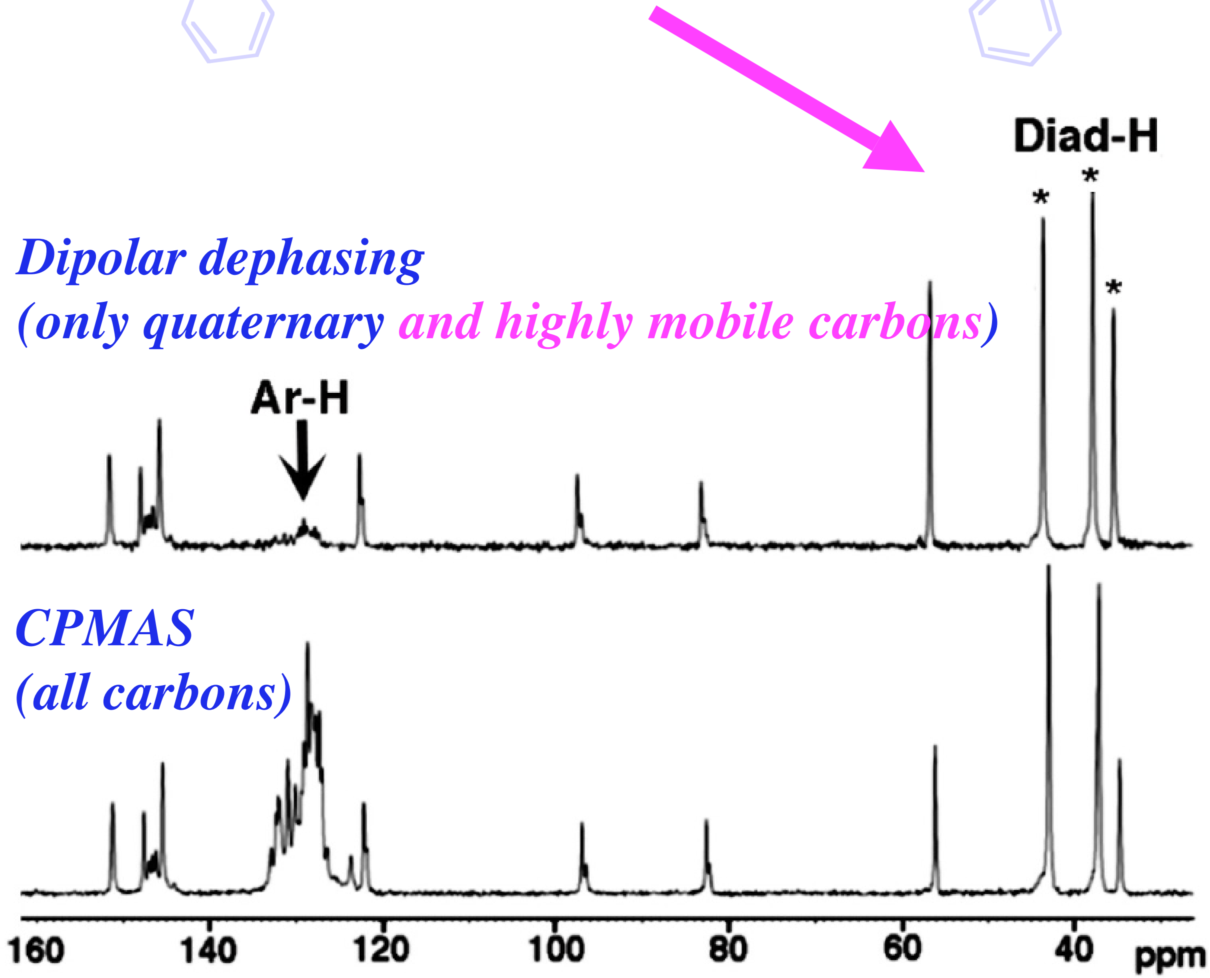
A Simple Insight into Rapid Diamantene Dynamics



CPMAS
(all carbons)





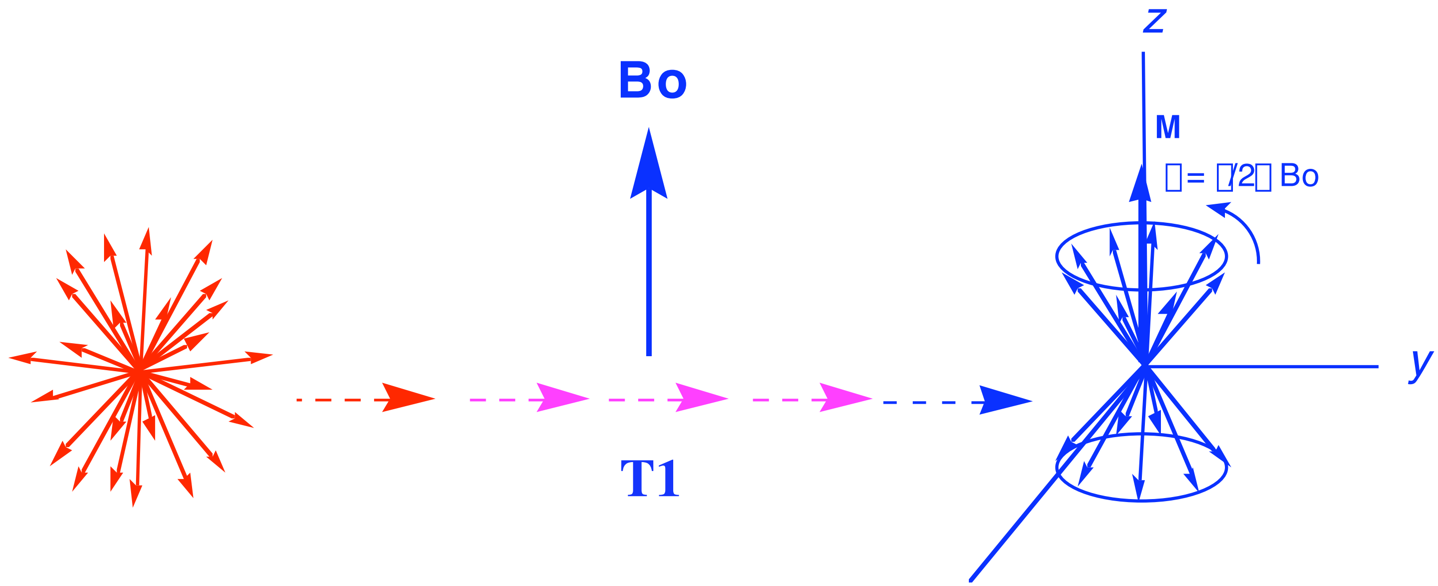


For a more quantitative method…

Spin Lattice Relaxation (T1)

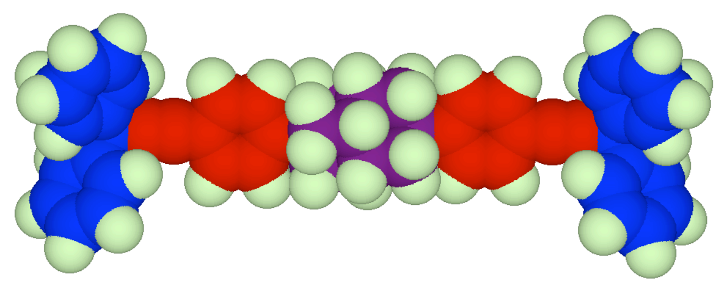
No Field => No Magnetization

Strong Field => Bulk Magnetization



SPIN LATTICE RELAXATION T1, is the time that it takes for M to reach its equilibrium value at Bo

- ***Spontaneous transitions would take thousands of years!***
- ***T1's are dominated by STIMULATED transitions, i.e., random local fields that oscillate at the Larmor frequency (ω_L) generated by the mechanical motion of nearby dipoles.***



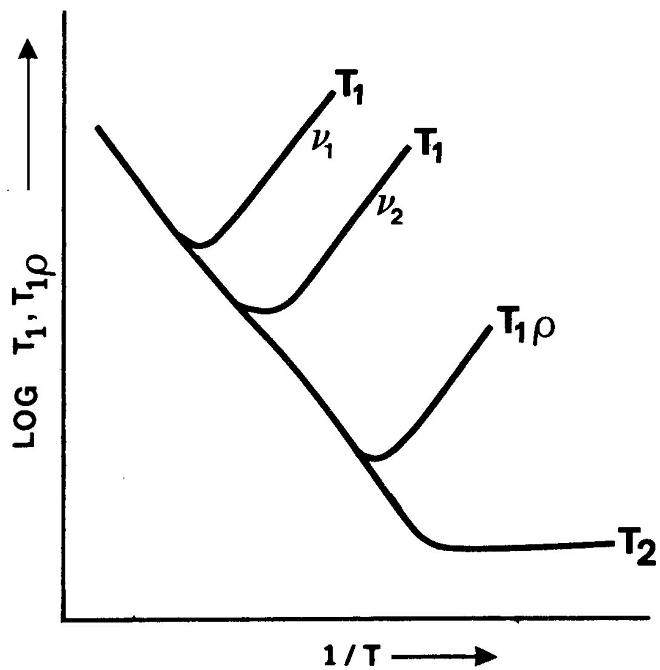
Spin-Lattice Relaxation

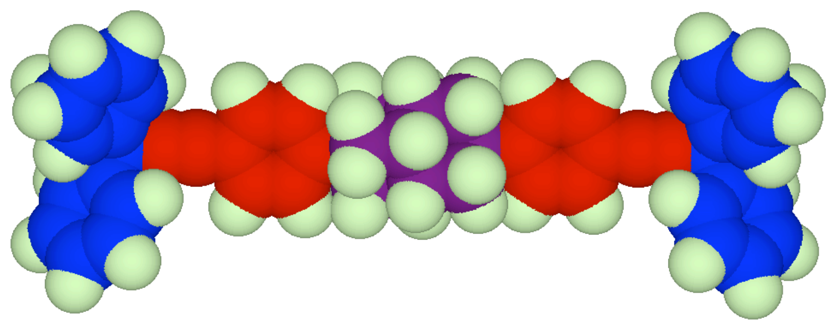
Kubo and Tomita relaxation expression:

Slope = $-E_a/R$ and $+E_a/R$
Minimum = $\omega_o \tau_c$

$$T_1^{-1} = C\ [\tau_c (1 + \omega^2 \tau_c^2)^{-1} + 4\,\tau_c (1 + 4\,\omega^2 \tau_c^2)^{-1}]$$

$$\tau_c = \tau_o \exp(Ea/kT)$$

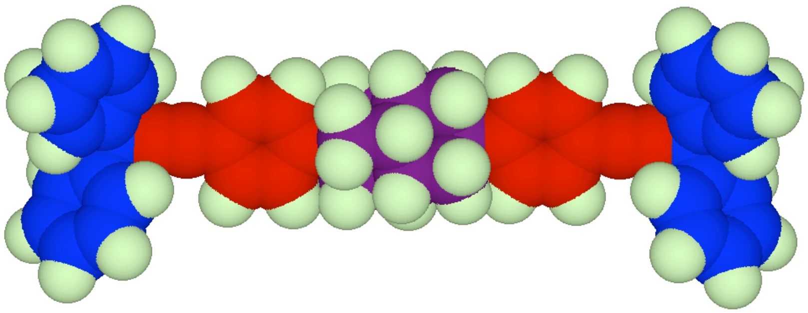


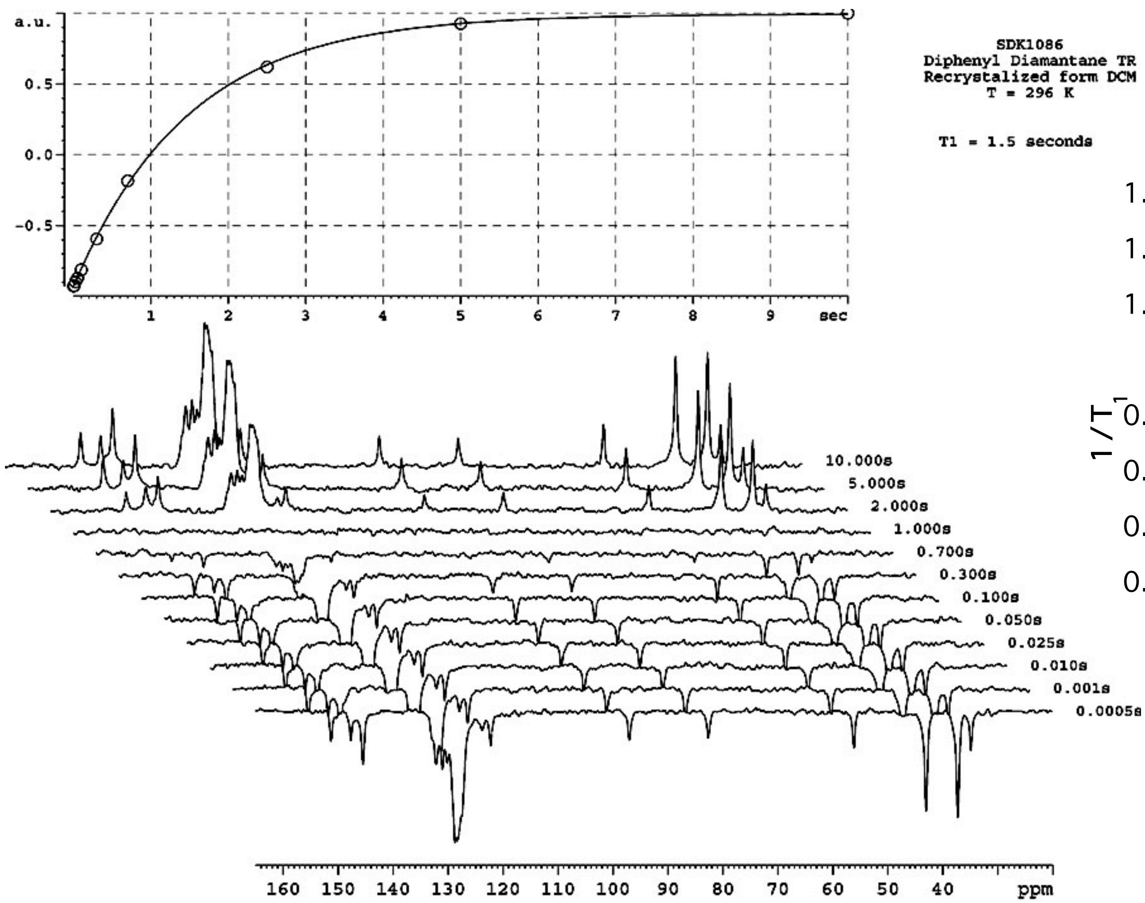


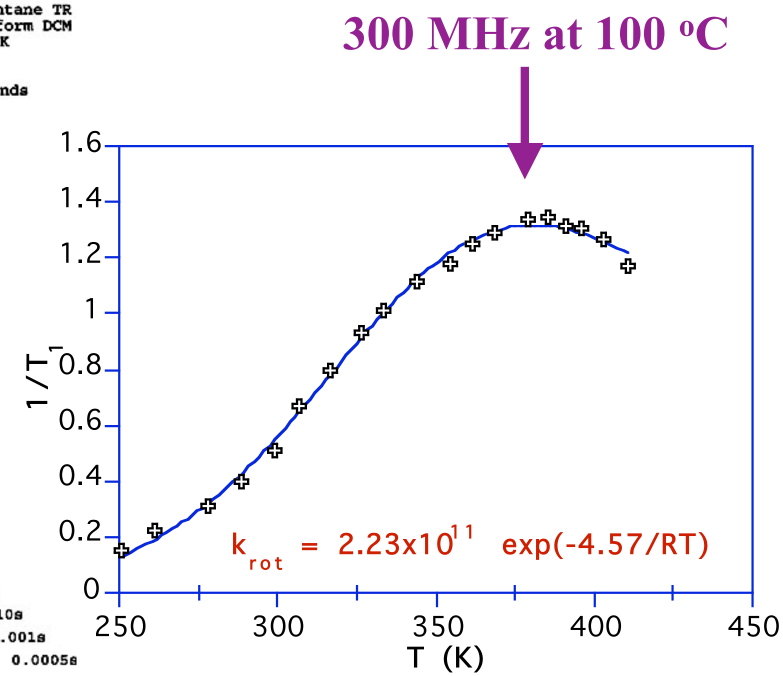
T_1 = Spin Lattice Relaxation
T_{1r} = Spin Lattice Relaxation in the Rotating Frame
T_2 = Spin-Spin Relaxation

Fyfe, Colin A. Solid State NMR For Chemists, C.F.C. Press, Guelph, Ontario, Canada, **1983**.

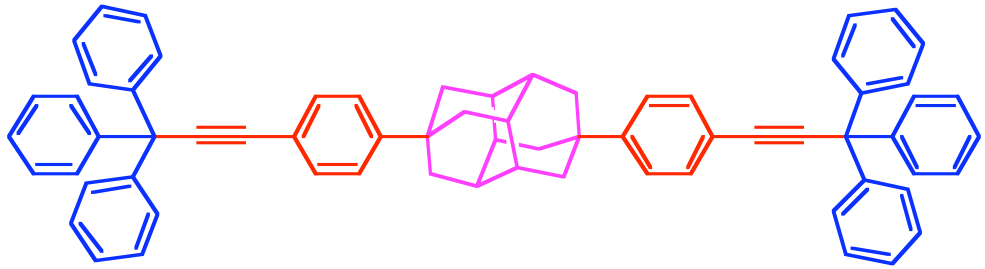
Gyroscopic Rotation By Spin-Lattice Relaxation



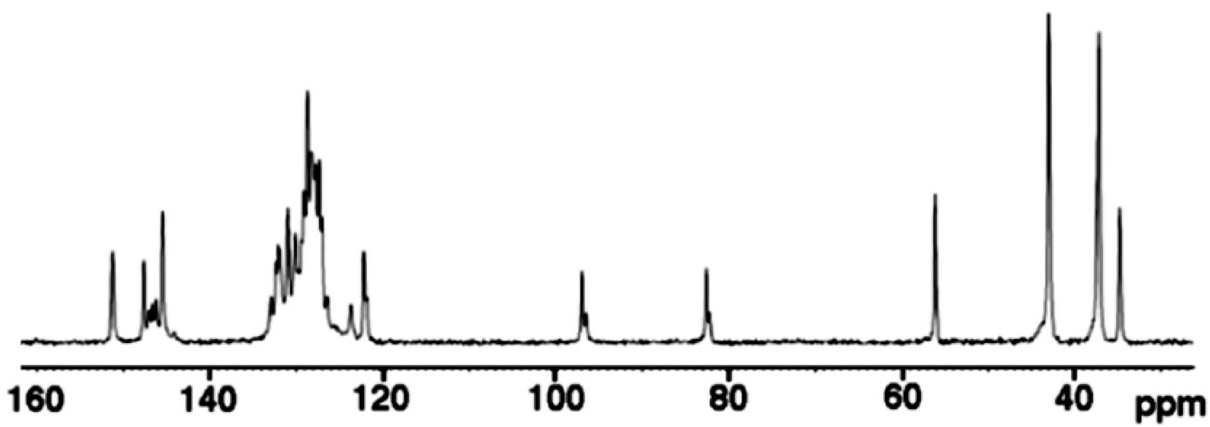


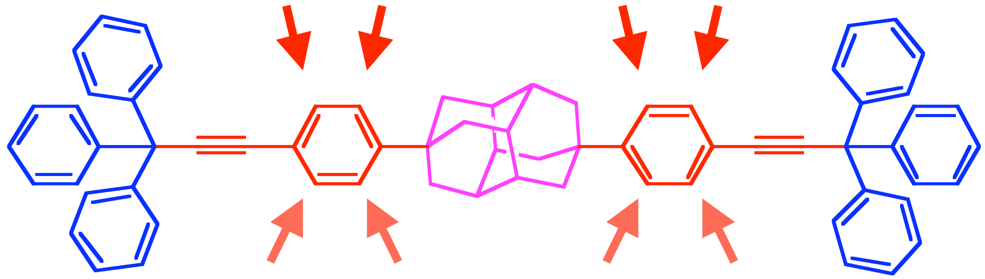


Only ~1.6 kcal/mol above the intrinsic barrier!

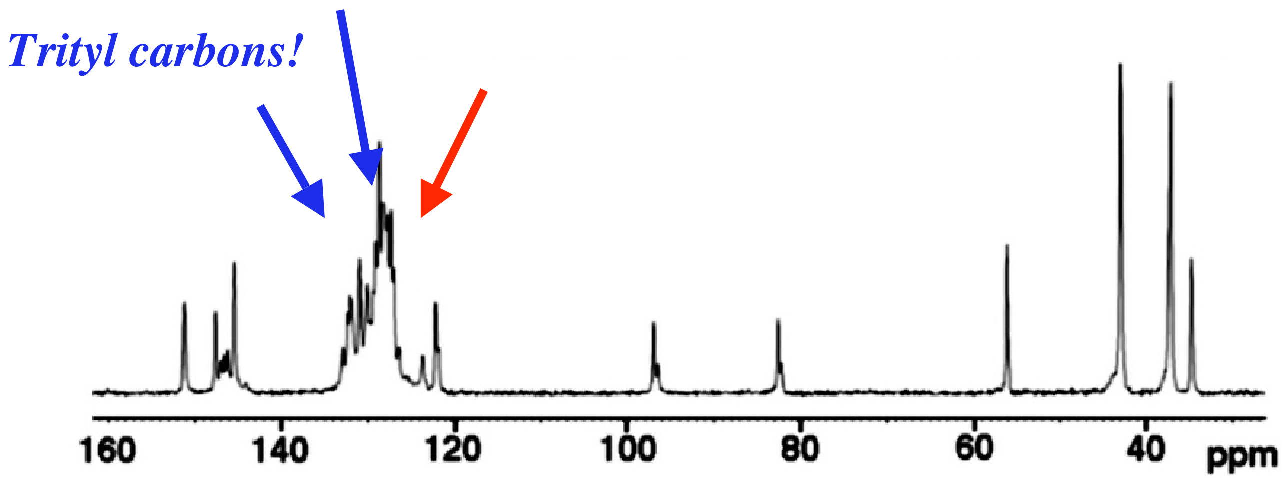


Can we use ^{13}C CPMAS VT-NMR coalescence methods to measure the rotation of the two phenylenes?



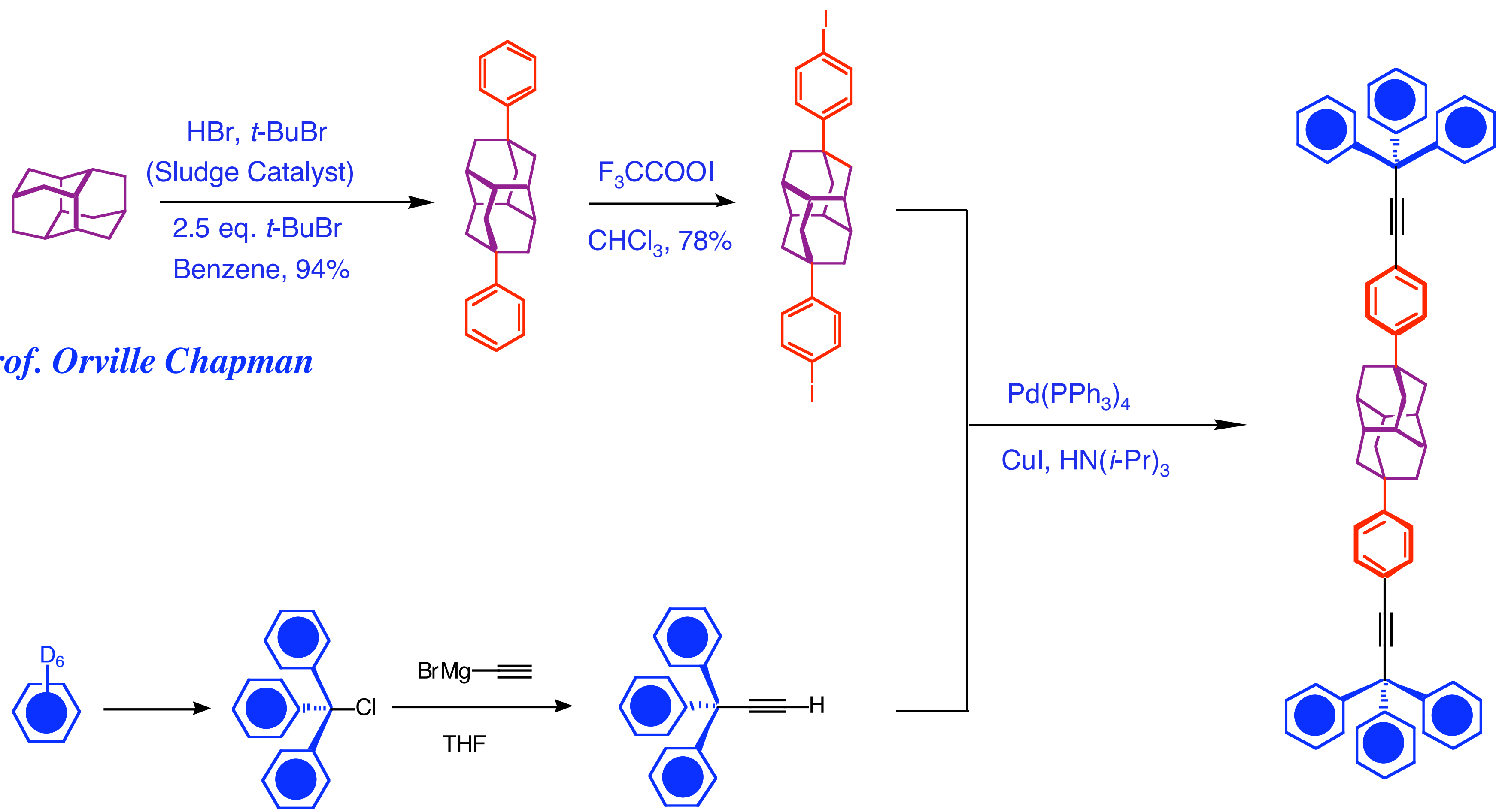


Can we use ^{13}C CPMAS VT-NMR coalescence methods to measure the rotation of the two phenylenes?



Organic Synthesis to the Rescue….

—Deuterate the trityl group… Detect only the ^{1}H-substituted PHENYLENES



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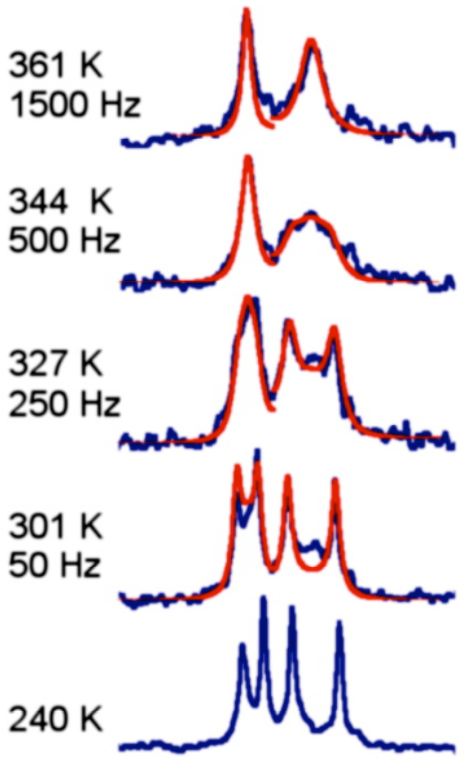
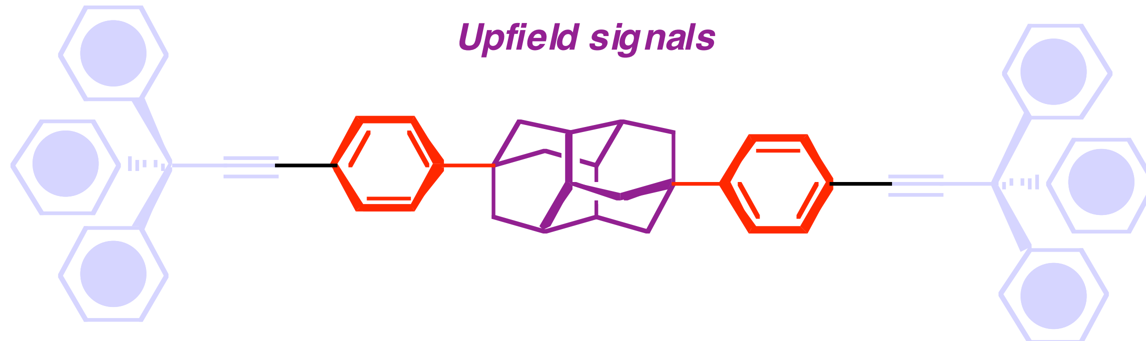
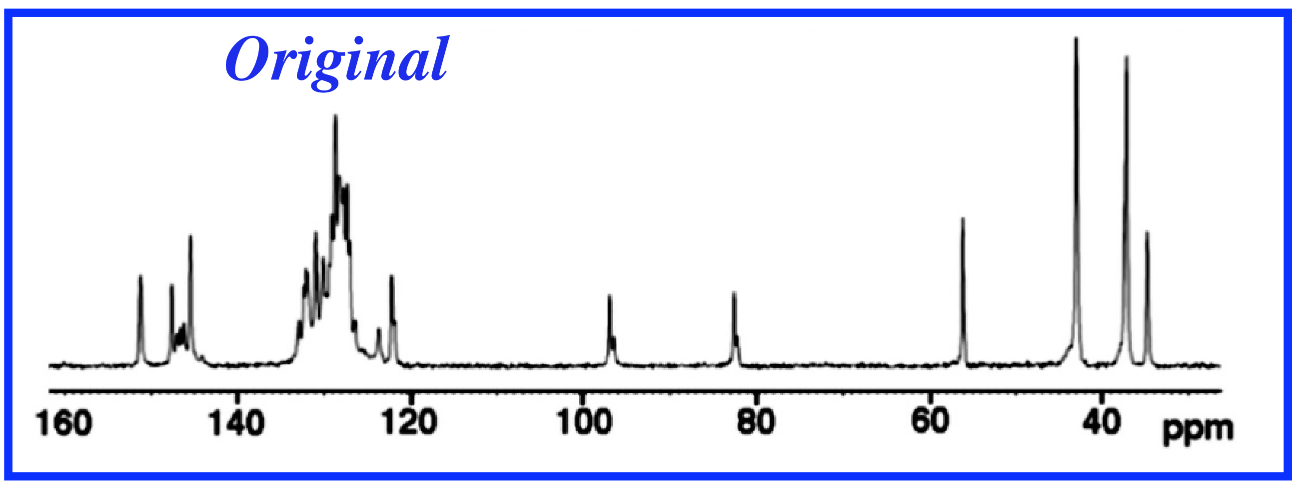
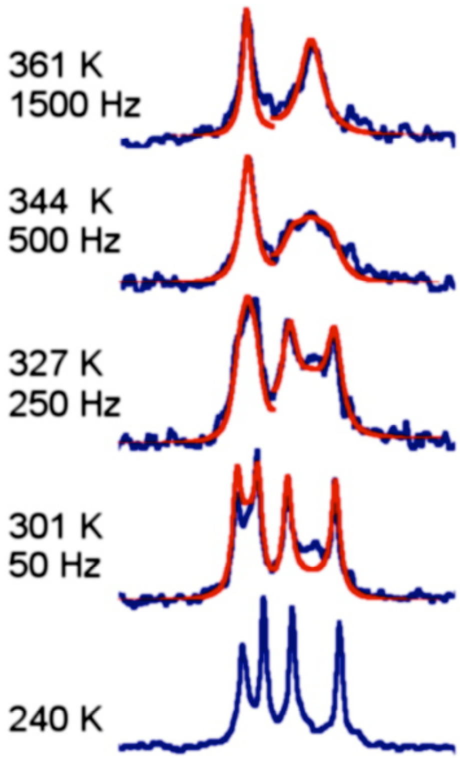
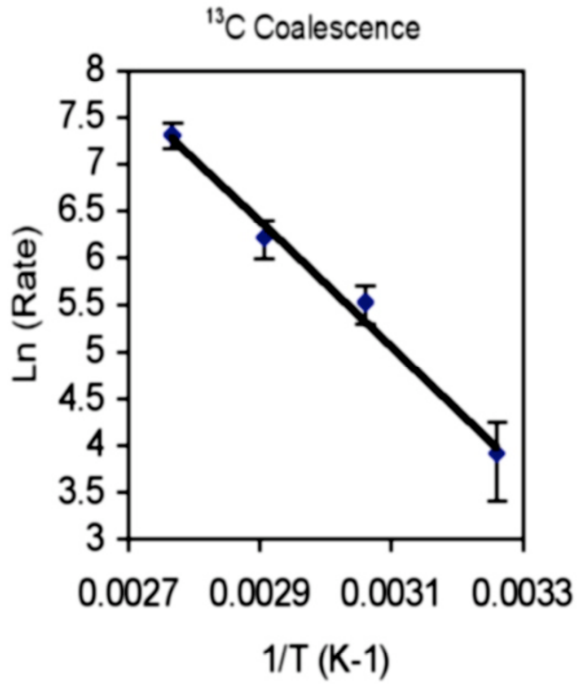

361 K
1500 Hz
344 K
500 Hz
327 K
250 Hz
301 K
50 Hz
240 K


Upfield signals

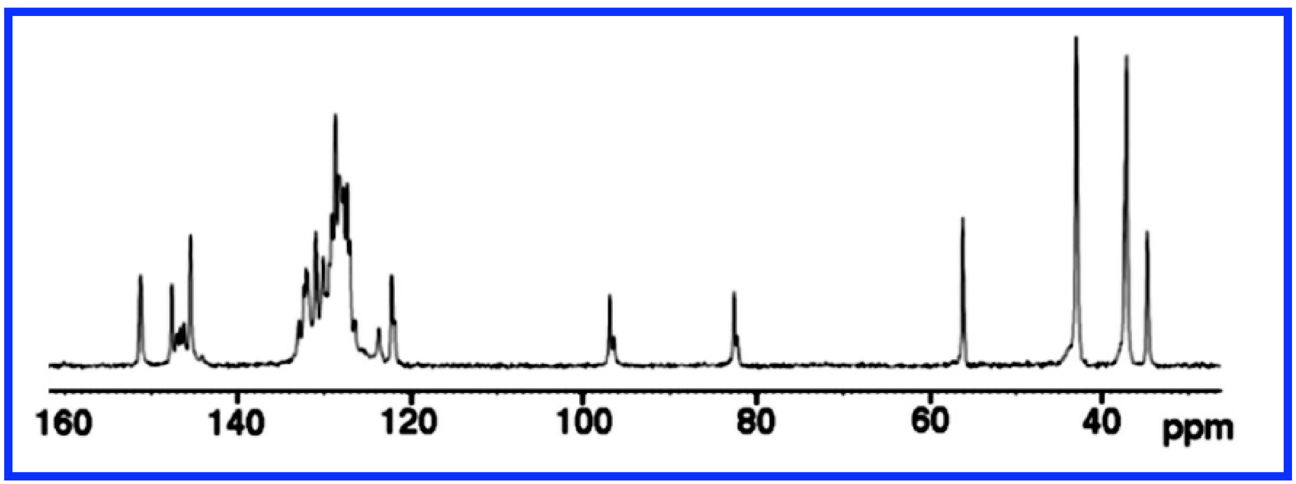

Original
160
140
120
100
80
60
40
ppm

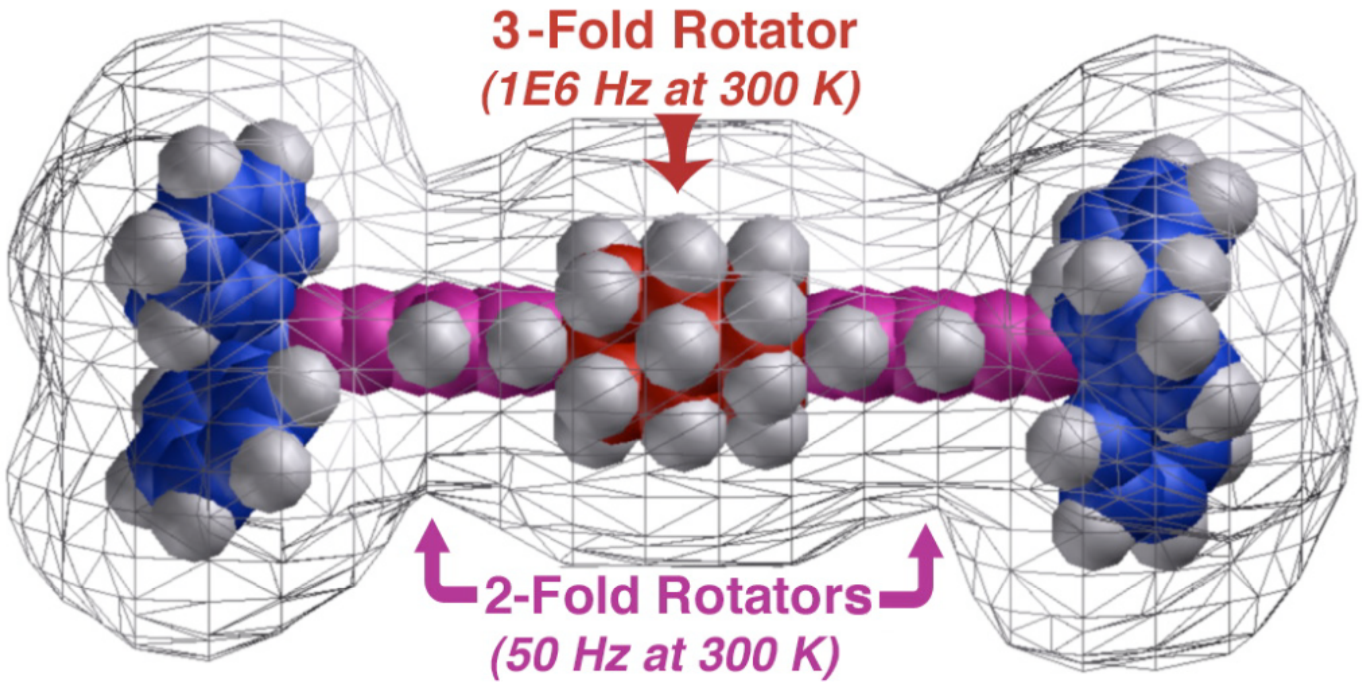




Ea = 13.7±1.1 kcal/mol

A = 5.1±4.5 x 10^{11} s^{-1}




3-Fold Rotator
(1E6 Hz at 300 K)
2-Fold Rotators
(50 Hz at 300 K)

Conclusions: ***Internal Dynamics in Crystals can be "Engineered" with Information Contained in Molecular Structures. Artificial Molecular Machines Can't be that Far***