M.A.(Tony) Whitehead
Chemistry Department
McGill
Molecular Orbital Modelling of Dendrimers & Nano-Tubes

REVIEW OF TALKS GIVEN AT:

Friday, 28th August, 2008
FAPPMS 2008, Three Rivers Quebec

Monday 15th, June, 2009
HPCS 2009 - Kingston, Ontario

Saturday 27th, June, 2009
ACA 2009, Montreal, Quebec
DRENDRITIC MOLECULES

Dr Ashok Kakkar

Rami Hourani

Ye Tien
Divergent Synthesis of DHBA-Based Dendrimers

\[ \text{Me}_2\text{Si(NMe)}_2 \rightarrow \text{DHBA} \]

(DHBA)

3,5-dihydroxybenzyl alcohol

Aggregate at cac

Higher generation number... more globular structures giving well defined internal cavities
Fig. 5. DG1, DG2, and DG3 structures with their relative sizes (diameters).
DLMO are orthogonal to all other DLMO and independent

DLMO are the same as DG1 in shape and energy:

DG 2  DLMO are the same as DG1 in shape and energy:
Fig. 2. The lowest unoccupied molecular orbitals (LUMO) of DG2 along with their numbers and energies.
Encapsulation of DR1 in DHBA-Based Dendrimers

Aggregation & Encapsulation

\[ \text{Disperse Red 1} \]

Disperse Red 1

Blue Shift in \( \lambda_{\text{max}} \) of DR1
Divergent Synthesis: TEB-Based Dendrimers

1,3,5 Triethynylbenzene (TEB)

Me$_2$Sn(NEt$_2$)$_2$ → (TEB)

Structures of TEB-Based Dendrimers

TOP VIEW

SIDE VIEW

1,3,5 Tri Ethynyl Benzene
Organometallic Dendrimers by Direct Replacement

An easy route to include transition metal centres in the dendrimers


M = Pd, Pt...

30%
DHBA

DG1

TEB

No Catalyst!

30%
PLATINUM
Using “Click” Chemistry To Build Dendrimers

1,3,5 Tri Ethynyl Benzene

\[
\begin{align*}
1,3,5 & \text{ Tri Ethynyl Benzene} \\
\text{TEB} & \\
\text{Sodium Ascorbate} & \\
\text{CuSO}_4 & \\
3.3 & \text{ eq.}
\end{align*}
\]
Using “Click” Chemistry To Build Dendrimers

Remove the silyl groups

Then continue to build from the triple bonds
DG 1

-0.205 au. lumo +2

Same DLMO shape

DG 2

-0.018au lumo+8
Centre: -0.317 a.u. homo-1
Left: -0.331 a.u. homo-4
Right: -0.325 a.u. homo-2
Bottom: -0.326 a.u. homo-3
SMI NANO TUBES

Dr. Theo van de Ven

Tom Lazzara
Figure 1: (a) Structure of SMA and SMI alternating copolymers. (b) Structure of the maleic anhydride monomer and the maleimide monomer before and after hydrolysis.
**Figure 3:** The SMI monomer (Hydrogens removed for clarity): comparison between the gas-phase PM3 (tube model) optimized structure and the DFT B3LYP 6-31G***( balls and bond model) solvated in water with HCl. The maleimide ring shows deviations (arrows) of 8° at the styrene and 20° at the maleimide.

**Figure 4:** Progression of the PM3 optimized polymer, from dimer to quadrimer. Arrows represent the orientation of the styrene monomers along the polymer backbone, which is perpendicular to the view plane shown.
Figure 5: Chiral sites in SMI polymers. Site 1 has an R or S chirality, while site 2 has a possible E or Z chirality. In SMA, site 2 does not restrict the linear conformation of the chain or the relative distribution of styrene monomers, but this is not the case for maleimide copolymers.

Figure 6: PM3 optimized isotactic SMI hexamer: sites 1 = S, sites 2 = E(SS). (left) lateral view (right) cross section view. The styrene groups are organized in the isotactic polymer and can associate through π-stacking. The angles formed by the maleimide and styrene ring are 110° and 70°.
Figure 7: Visual representation of the NoChain model for a quadrimer (lighter atoms are further behind). Left, SMI quadrimer with chains; Right, SMI quadrimer without chains; NoChain Model. The styrene and maleimide monomers are slightly more disordered but the bulk of the structure is preserved without the chains.
Figure 8: Left: The chiral sequence in “balls and bond” model, is for an isotactic quadrimer with a chiral sequence \(Z(SS)^3 S^3\). In the “tube” model, the end chirality is changed from \(E\) to \(Z\), showing \(E(SS)^2 S^2 Z(RS)\) \(S\) chiral sequence. Terminal styrene monomer is rotated by 180° (circles \(E\) to \(Z\)) and the polymer backbone tilts by 45° (arrows). Right: A random chiral sequence for an hexamer, showing a linear configuration but no symmetry, styrene monomers overlap maleimide monomers in this cross-section view.
Figure 10: Association geometries between isotactic SMI hexamers. From left to right: shown are the cartoons of cross-section views, the tube models along with the herringbone arrangements of the styrene monomers for each association geometry.
Fragment of PM3 minimum energy Head-to-Tail association

HOMO: DLMO 161

Electrostatic Potential Surface
60° Lower π-π stabilization, higher maleimide chain interactions

Figure 3: Stabilization energy, plotted as a function of inter-polymer distance (Å) and association angle for the Head-to-Head association between SMI polymers. The minimum association differs slightly for different angles due to chain-chain interactions and is about 12-13 angstroms.
Figure 6: Organization of a sheet of SMI polymers into a nanotube structure. This structure offers the highest stabilization energy for the association between SMI polymers, forming a closed system between hydrophobic ends. (a) The nanotube has an octagon shape, made from 8 isotactic SMI polymer in the Head-to-Head conformation. (b) SMI nanotube shown with van der Waals radii, used to approximate the outer and inner diameter.
Figure 7: proposed growth mechanism for SMI nanotubes. SMI polymers can self-assemble at the edges of an initially closed structure and gain in stabilization energy from the ordered association because free styrene monomers are available for π-stacking. The nanotube grows in a spiral. (lighter colour atoms are further behind the plane of view)
CONCLUSIONS

Using insight and care and understanding the weaknesses of the theories and programmes

1. Theory gave insight into dendrimer structures

2. Theory predicted possible metal containing dendrimers

3. Theory predicted nano-structures which were made

4. Theory helped to analyse the problems of SMI nano-structures and led to synthetic methods
END
WATER ON CALCITE AND ARAGONITE

Water on Calcite breaks the Ca-O bond

Joseph Kinghorn-Taenzer

Intakhab Alam Zeeshan
ARAGONITE

CRYSTAL

Side view

DOUBLE LAYER

SINGLE LAYER ATOMS FIXED
2H₂O SIDE and TOP pictures show 1) no bonds broken in the Aragonite Double Layer 2H₂O lean closer to the surface
4H$_2$O SIDE and TOP (1) and (2)
Pictures show no bonds broken in the Aragonite Double Layer
4H$_2$O arrange their H atoms to avoid each other
Average Valence Bond H-bond distance = 1.97Å

-1.045 HOMO +152

O...H = 1.067Å

H-bond = 2.489Å
-1.054 au HOMO +146
O..H = 1.005Å; H-bond=2.579Å

-1.085 au HOMO +118
O..H=1.53Å9; H-bond=2.578Å

-1.086 au HOMO +117
O..H=1.068Å; H-bond=2.429Å

-1.088 au HOMO + 116
O..H=0.977Å; H-bond=2.986Å
-1.091 au HOMO+115
O..H=1.005 Å; H-bond=2.577 Å
DOUBLE LAYER: FOUR H$_2$O

Both water H (H$_1$, H$_2$) are bonded to different O$_{\text{surface}}$

$-0.614 \text{ au HOMO}+289$

$O..H_1=0.986 \text{Å}; \ H\text{-bond}=2.731 \text{Å}$

rotate to show H-bond

$-0.617 \text{ au HOMO}+288$

$O..H_2=0.982 \text{Å}; \ H\text{-bond}=3.79 \text{Å}$
Both Hydrogen Bonds at the end CaO are in the same DLMO 268

-0.676au HOMO+268

LEFT O..H=1.027Å; H-bond=2.453Å

RIGHT O..H=1.052Å; H-bond=2.395Å
1) Prediction of 3D structures of organic and Sn and Pt dendrimers

2) Prediction of the form of nano tubes from SMI

3) Prediction that unlike calcite which dissolves in Water, Aragonite forms weak H-bonds and does not dissolve.
THEORETICAL METHODS FOR CALCULATIONS

1 Molecular Mechanics: Balls and Springs

2 Quantum Mechanics

Classical Conservation of Energy

\[ \frac{1}{2}mv^2 + \frac{1}{2}kx^2 = E \]

Newton’s Laws

\[ F = ma = -kx \]

Quantum Conservation of Energy

\[ H = \frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + \frac{1}{2}kx^2 \]

Schrodinger Equation

\[ \psi(\vec{r}) = \sum \psi_n(\vec{r}) \phi_n(\vec{r}) \]

Energy becomes the Hamiltonian operator

Wavefunction

\[ \hat{H}\Psi = \hat{E}\Psi \]

Energy “eigenvalue” for the system.

The form of the Hamiltonian operator for a quantum harmonic oscillator.

2a Density Functional theory; \( n^3 \)

\[ V_s = V + \int \frac{e^2n_s(\vec{r}')}{|\vec{r} - \vec{r}'|} \, d^3r' + V_{XC}[n_s(\vec{r})], \]

3 Molecular Dynamics

Newtonian Dynamics

\[ \dot{\vec{r}} = \frac{\vec{p}}{m} \]

\[ \dot{\vec{p}} = -\hbar^2 \frac{\partial^2}{\partial x^2} + \frac{1}{2}kx^2 \]

\[ V = V_H + V_b + V_{tor-i} + V_{tor-p} + V_C + V_{vdW} \]

\[ V_H = \frac{1}{2} \sum_{n} K_{Hn}(r_n - r_o)^2 \]

\[ V_b = \frac{1}{2} \sum_{n} K_{\theta n}(\theta_n - \theta_o)^2 \]

\[ V_{tor-i} = \frac{1}{2} \sum_{n} K_{\xi n}(\xi_n - \xi_o)^2 \]

\[ V_{tor-p} = \frac{1}{2} \sum_{n} K_{\phi n}[1 + \cos( m\phi_n - \delta_n)]^2 \]

\[ V_C = \frac{1}{4\pi\epsilon_0} \sum_{i<j} \frac{q_i q_j}{r_{ij}} \]

\[ V_{vdW} = \sum_{i<j} \left[ \frac{C_{12}(y)}{r_{ij}^{12}} - \frac{C_6(\vec{r})}{r_{ij}^6} \right] \]
Research Supported:
The NSERC (CANADA): Discovery Grant
Summer Undergrad Research Student 2008:
  Intakhab Alam Zeeshan

Le Fonds québécois de la recherche sur la nature et les technologies.

Doctoral Scholarships:
Tom Lazzara, 2007       Rami Hourani, 2007

Centre for Self-Assembled Chemical Structures:
Summer Undergrad Research Award, 2008
  Ye Tian:

SIGMA XI: Grant in Aid of Research:
  Tom Lazzara, 2007
  Rami Hourani, 2007