

September CUME

Organic Chemistry

Department of Chemistry
University of Missouri—Columbia
Saturday, September 27, 1997
@Nine O'Clock
Chemistry Reading Room

Dr. Rainer Glaser

Announced Reading

“Modern Hydrocarbon Chemistry”

Angewandte Chemie Int. Ed. Engl. **1997**, 36, issue 15.

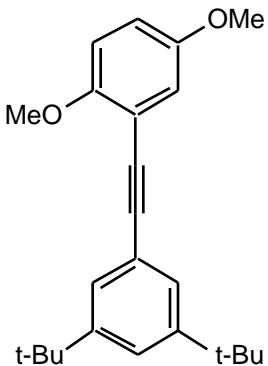
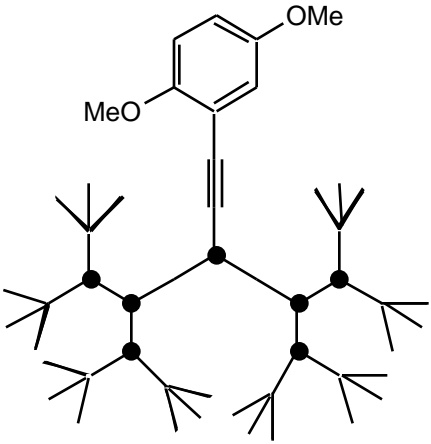
Suggested reading includes the Nobel Lectures by Kroto, Smalley, and Curl.

Question 1. Anomalous Shift in the Fluorescence Spectra of a High-Generation Dendrimer in Nonpolar Solvents. (35 points)

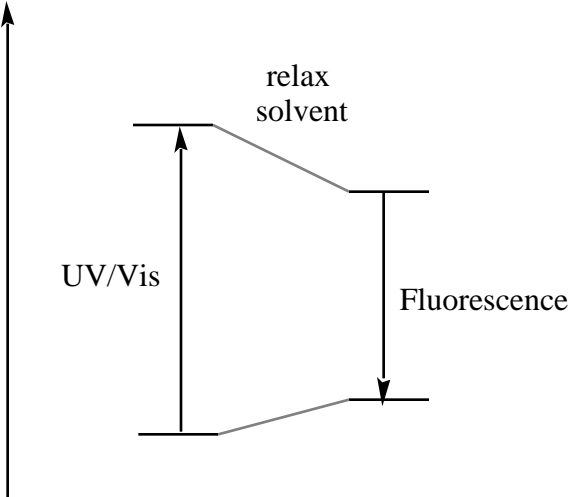
Devadoss, C.; Bharathi, P.; Moore, J. S. *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 1633-1635.

The fluorescence spectra are discussed for a series of dendrimers as a function of the dendrimer generation. Let's make sure we know what structures we are talking about, let's look at the solvent dependency of fluorescence for a simple dye, and then let's take a look whether there really is something "anomalous" about Moore's system.

(a) Moore's basic system is molecule **1**, a tolane which carries two methoxy groups on one of the benzene rings and two bulky alkyl groups in the other aromatic ring. To simplify the structural drawings, Moore came up with his own rules for drawing these dendrimers. For **1**, the molecule is given and I want you to draw the molecule in Moore's symbolic notation. For **2**, the molecule is given in Moore's symbolic notation and I want you to draw the full structure. (10 points)

<p>Actual structure of 1:</p> 	<p>Symbolic Structure of 1:</p>
<p>Actual structure of 2:</p>	<p>Symbolic Structure of 2:</p> 

(b) Now let's take the fluorescence spectrum of a simple dye and let's consider how that spectrum is affected by the solvent. Draw the "neutral" resonance form **I** of *para*-nitroaniline, PNA. Then draw the "polar" resonance form **II** of PNA (the "through-conjugated" one). Both of these resonance forms are used to describe the ground state (GS) of the molecule as well as its excited state (ES). The difference is simply that the ground and excited states have very different contributions from both of these resonance forms. In the appropriate place, state which resonance form dominates the GS and the ES. Considering the dominant resonance forms for GS and ES, state which state has the higher dipole moment. In the diagram, the energy levels are shown for the UV/Vis absorption and for the fluorescence. Explain why the fluorescence is red-shifted relative to the absorption. Explain why the red-shift usually increases with the polarity of the solvent. Feel free to draw cartoons describing the solvation at the four levels. (15 points)

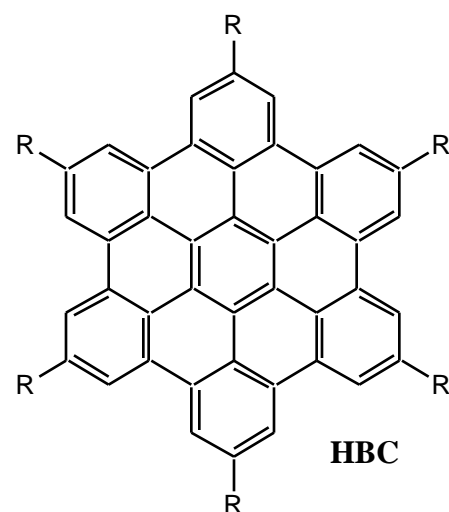
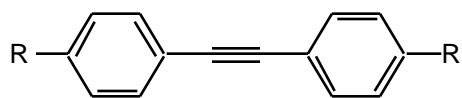
Neutral form I :	Polar form II :
I dominates the _____ (GS, ES) and II dominates _____ (GS, ES).	Among GS and ES, the state _____ (GS, ES) clearly has the higher dipole moment.
	Explain the red-shift of the fluorescence compared to the absorption:
Explain the red-shift with increasing solvent polarity:	

(c) Moore et al. found that their 5th generation dendrimer, the 63mer, shows an “anomalous” bathochromic shift when the solvent is changed from cyclohexane (380 nm) to pentane (421 nm). The polarity of the solvent obviously is not a factor. Discuss possible reasons for this “unusual” observation. Briefly describe qualitatively the reasons for the observed solvent dependency which were discussed by Moore et al. Also discuss possible ways in which the solvent might affect the change of the dipole moment of the dendrimer upon excitation. (10 points)

Question 2. Polycyclic Aromatic Hydrocarbons by Cyclodehydrogenation and Skeletal Rearrangement of Oligophenylenes. (35 points)

Müller, M.; Iyer, V. S.; Kuebel, C.; Enkelmann, V.; Müllen, K. *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 1607-1610.

(a) Outline a synthesis of hexa-*peri*-hexabenzocoronene (HBC) from *para*-substituted tolane. Show the structure of the hydrocarbon (HPhB) formed initially. Provide reagents and state the reaction mechanism for each of the two steps. If you have not read how the synthesis actually was accomplished, I would be interested in a proposal of this synthesis. Answer the questions on the bottom of this page.

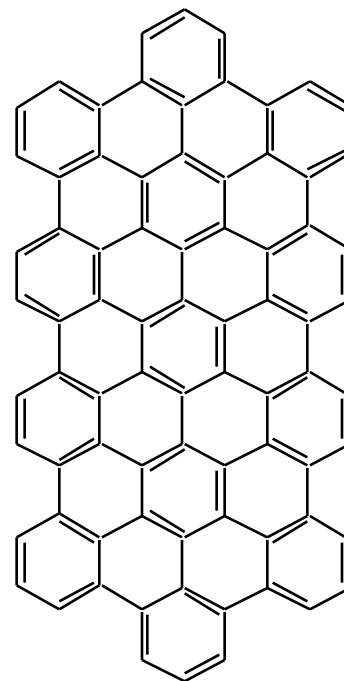
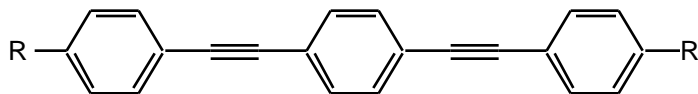


For R=H, how many signals are there in the H-NMR of HBC.

For R=H, how many signals are there in the ^{13}C -NMR of HBC?

For R=H, will the chemical shift of the H-atoms in HBC be higher or smaller than in benzene?

(b) The polybenzenoid $C_{78}H_{26}$ hydrocarbon was synthesized by Müllen et al. starting from 1,4-di(phenyl)ethynylbenzene using Diels-Alder chemistry involving tetracyclone. Show the structure of the hydrocarbon formed initially. Provide reagents and state the reaction mechanism for each of the two steps. If you have not read how the synthesis actually was accomplished, I would be interested in a proposal for this synthesis.



How many signals are there in the H-NMR of $C_{78}H_{26}$.

How many signals are there in the ^{13}C -NMR of $C_{78}H_{26}$?

For $R=H$, will the chemical shift of the H-atoms in $C_{78}H_{26}$ be higher or smaller than in benzene?

Question 3. Nobel Lectures on Fullerenes. (30 points)

(a) Dawn of the Fullerenes: Conjecture and Experiment. Robert F. Curl *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 1567-1576.

(b) Symmetry, Space, Stars, and C₆₀. Harald Kroto *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 1579-1593.

(c) Discovering the Fullerenes. Richard E. Smalley *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 1595-1601.

(a) Allotropy (2+4+2+2=10 points)

Define the term “allotrope” precisely.

Give the names of all allotropes of carbon.

Which one of the carbon allotropes is the most stable one under standard conditions?

Name one element other than carbon that also forms “allotropes” and specify at least two of these allotropes.

(b) Curl conjectured about endohedral complexes of fullerene. Buckminsterfullerene has a cavity of almost _____ Å (provide the value if you know it, provide a reasonable estimate otherwise) in diameter. The La atom was one of the first ones to be placed inside of C₆₀. How was La@C₆₀ prepared and how was it detected? Be clear about the charge of the system. (2+4=6 points)

(c) Having read the three Nobel Lectures, describe your recollections concerning separation techniques (stay qualitative) and the spectroscopic characterizations of C_{60} (as detailed as you like). Say something about MS, of course, and then write what you know about the ^{13}C -NMR (how many peaks, what shift), IR (how many peaks, where) , and UV/Vis (color) spectra.

(d) Smalley writes that “carbon has this genius of making a chemically stable two-dimensional, one atom thick membrane in a three-dimensional world. And that, I believe, is going to be very important in the future of chemistry and technology in general.” He goes on to tell about the (10,10) fullerene nanotube. What is this (10,10) fullerene nanotube? Describe its structure (draw it if you dare). How are these tubes made? Why are these tubes better than wider tubes? Say as much as you can recollect.