Soot Formation From Coal Tar Surrogates Under Gasification Conditions

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Outline

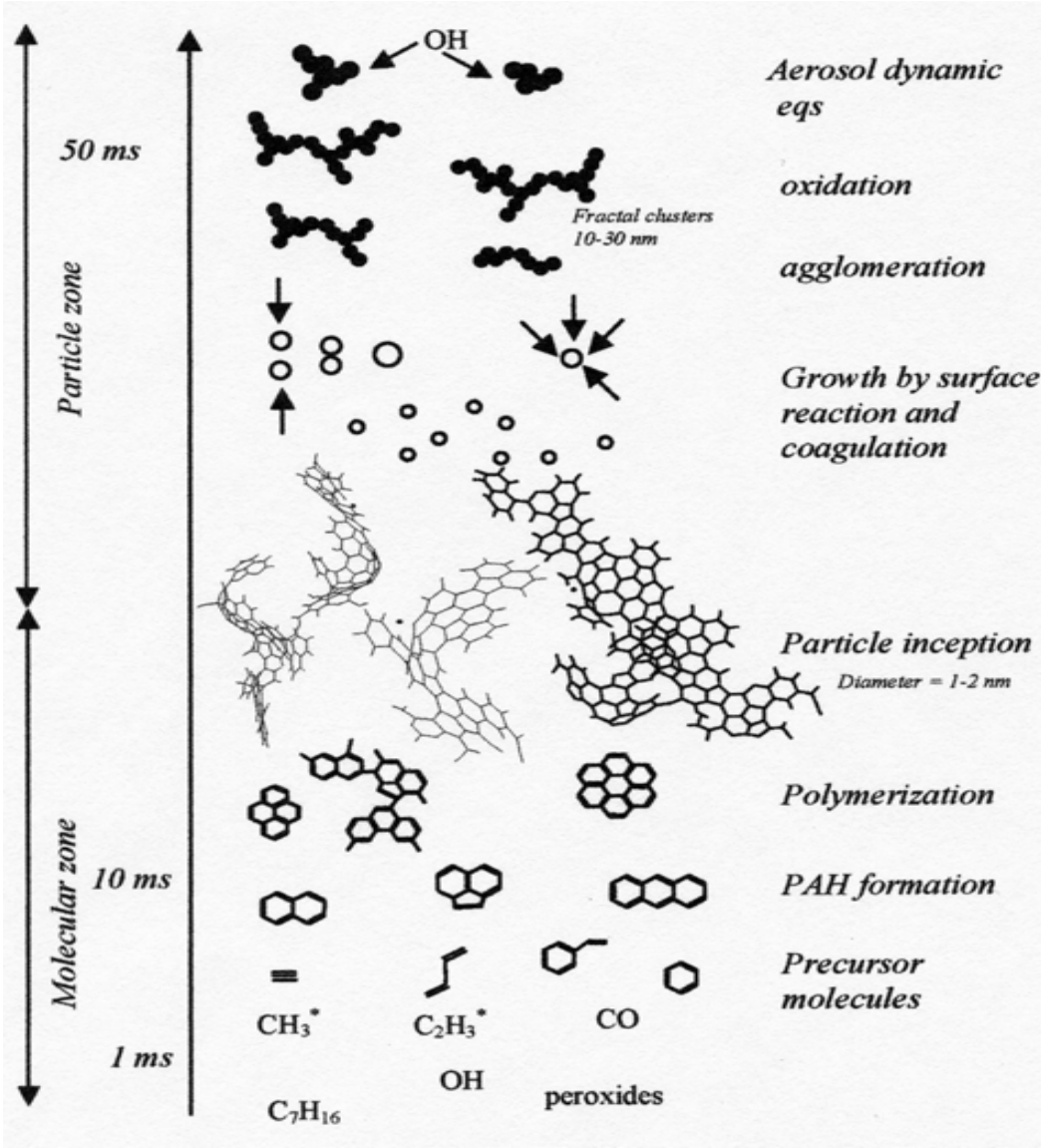
- Why study soot in coal gasification?
- Overview of soot formation processes
- Review of coal tar characteristics
- Model compounds studied
- Overview of experiments
- New facilities for future work at high pressure
- Findings with model compounds

Why Study Soot in Coal Gasification?

- Soot in flame regions can radiate significant amount of heat away from flame
- Increased pressure increases soot formation
- Soot may be more difficult to gasify than coal char

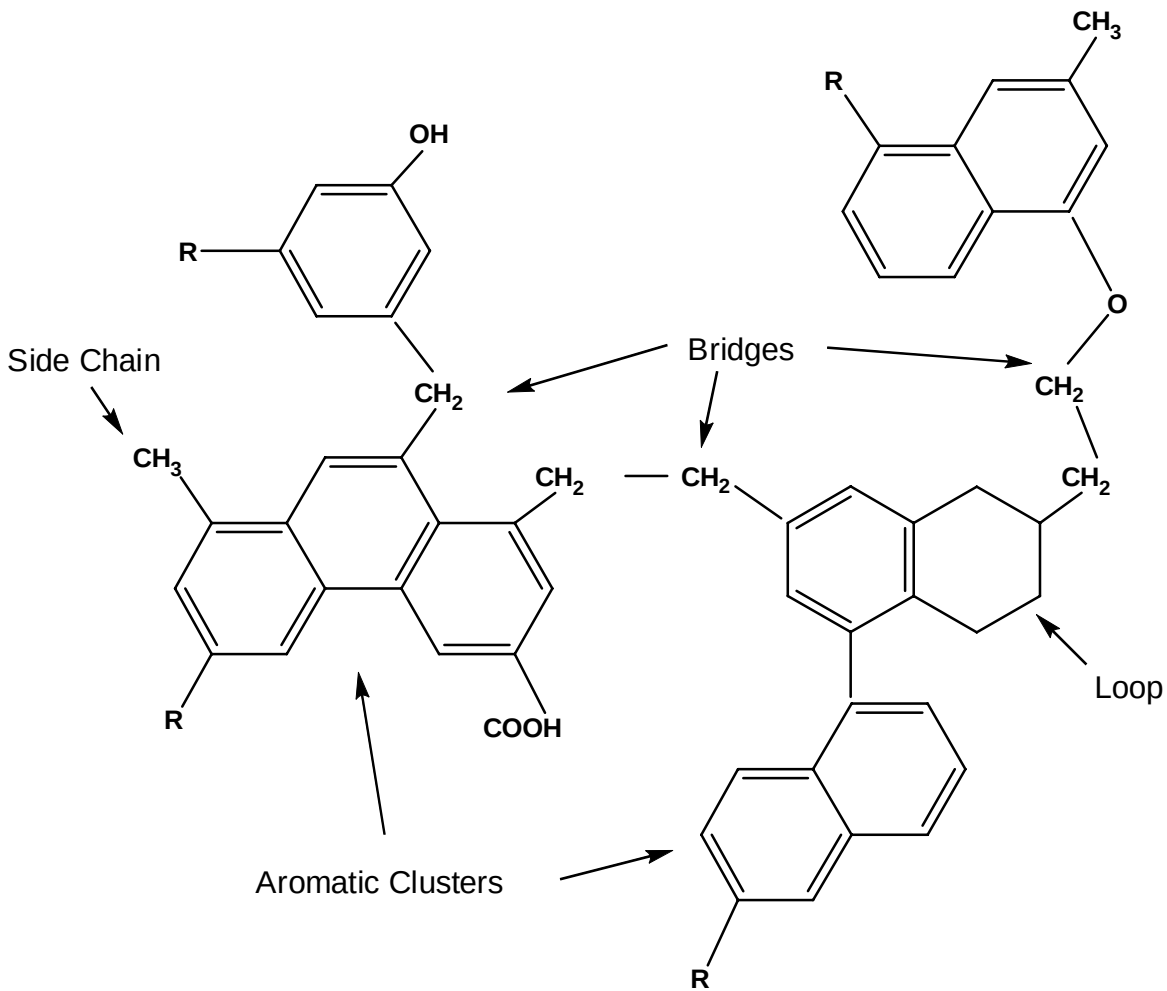
Soot Formation Process

- Reactants & products during combustion of light hydrocarbons
- HACA mechanism used
  - H abstraction, C addition



Sarofim, Longwell, Wornat, Mukherjee,, *Springer Series in Chemical Physics*, **1994**, 59, 485-99.

Representative Coal Molecule



- Aromatic clusters
- Bridges
- Side Chains

Characteristics of Coal Tar

- Product of primary pyrolysis, precursor of soot in secondary pyrolysis
- Elemental composition:
  - 78-82% C, ~4% H, ~1.7% N, 5-16% O, some S
- MW: Average of ~350 amu
- Carbons per cluster: C_{cl} = 11-17 (i.e., 3-4 rings)
  - Slightly lower than parent coal (13-15)
  - Clusters with higher vapor pressures evaporate preferentially during pyrolysis
- Aromaticity: $f_{a'}$ = 63-76%
  - $f_{a'}^{tar} \geq f_{a'}^{coal}$

Freihaut, J. D., W. M. Proscia and D. J. Seery, Energy & Fuels 3, 692-703 (1989)

Perry, et al., Proc. Combust. Inst., 28, 2313-2319 (2000)

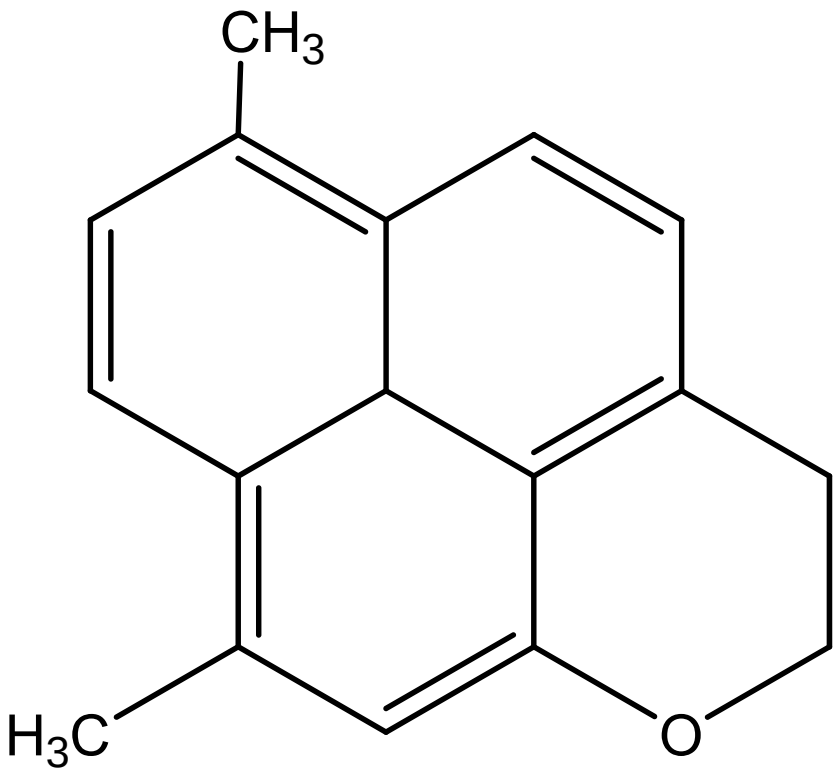
Characteristics of Coal Tar

- Cluster Molecular Weight (MW_{cl}):
  - ~240-290 amu
  - 38-44% below coal MW_{cl}
- Side-chain Molecular Weight (MW_{att}):
  - ~20-31 amu
  - Lower than parent coal value by 5-7 amu
  - Greater than char value
- Attachments per cluster/coordination # ($\sigma + 1$):
  - Typically ~4
    - ~2 bridges and ~2 side chains
  - Lower than parent coal and char (~4-6)

Perry, et al., Proc. Combust. Inst., 28, 2313-2319 (2000)

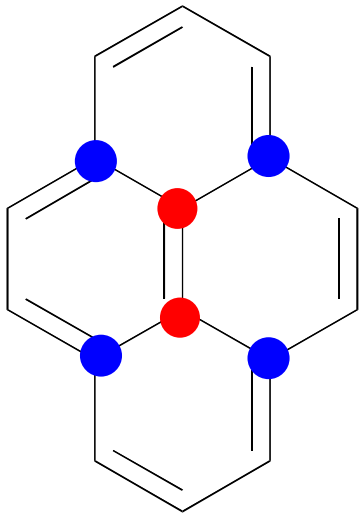
Watt, M. et al., 26th Symp. (Int.) on Comb., 3153-3160 (1996)

Suggested Average Tar Molecule

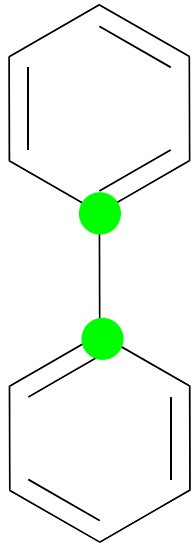


- MW = 235
- 3 aromatic rings
- C aromaticity = 0.76
- 2 side chains,
  2 bridges
- C content = 87%
- H content = 6.4%
- O content = 6.8%

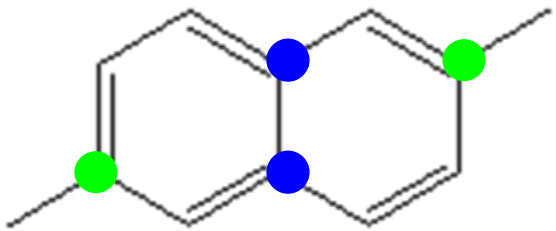
Model Compounds Selected



Pyrene



Biphenyl



2,6-dimethylnaphthalene

Carbon types

- Inner Bridgehead
- Outer Bridgehead
- Substituted

Experimental Methods and Conditions

- **Pyrolysis Conditions**
  - **Flat flame burner described by Fletcher in:**

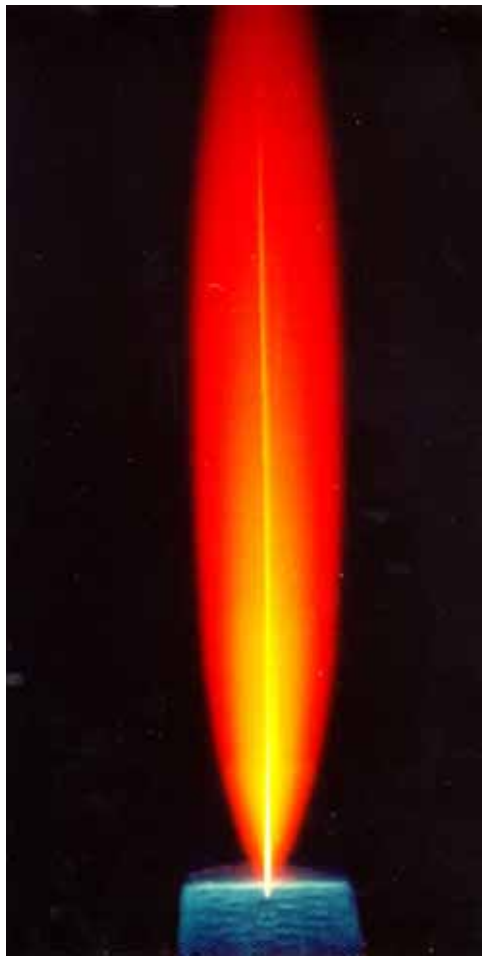
    Solum, Sarofim, Pugmire, Fletcher, Zhang, Energy & Fuels, **2001**, 15, 961-971.
- **Analytical Data**
  - **Electron Spin Resonance data was obtained on a Bruker x-band spectrometer**
  - **Solid-state ^{13}C NMR data was obtained according to standard methods developed at the Utah NMR facilities as described in:**

    Solum, Sarofim, Pugmire, Fletcher, Zhang, Energy & Fuels, **2001**, 15, 961-971.; Winans, Tomczyk, et. al., Energy & Fuels, 2007, 21, 2584-2593
  - **GC/MS and High Resolution MS (HRMS) techniques including hydrogen deficiency analysis (on CH_2Cl_2 extracts) are given in:**

    Winans, Tomczyk, et. al., Energy & Fuels, 2007, 21, 2584-2593

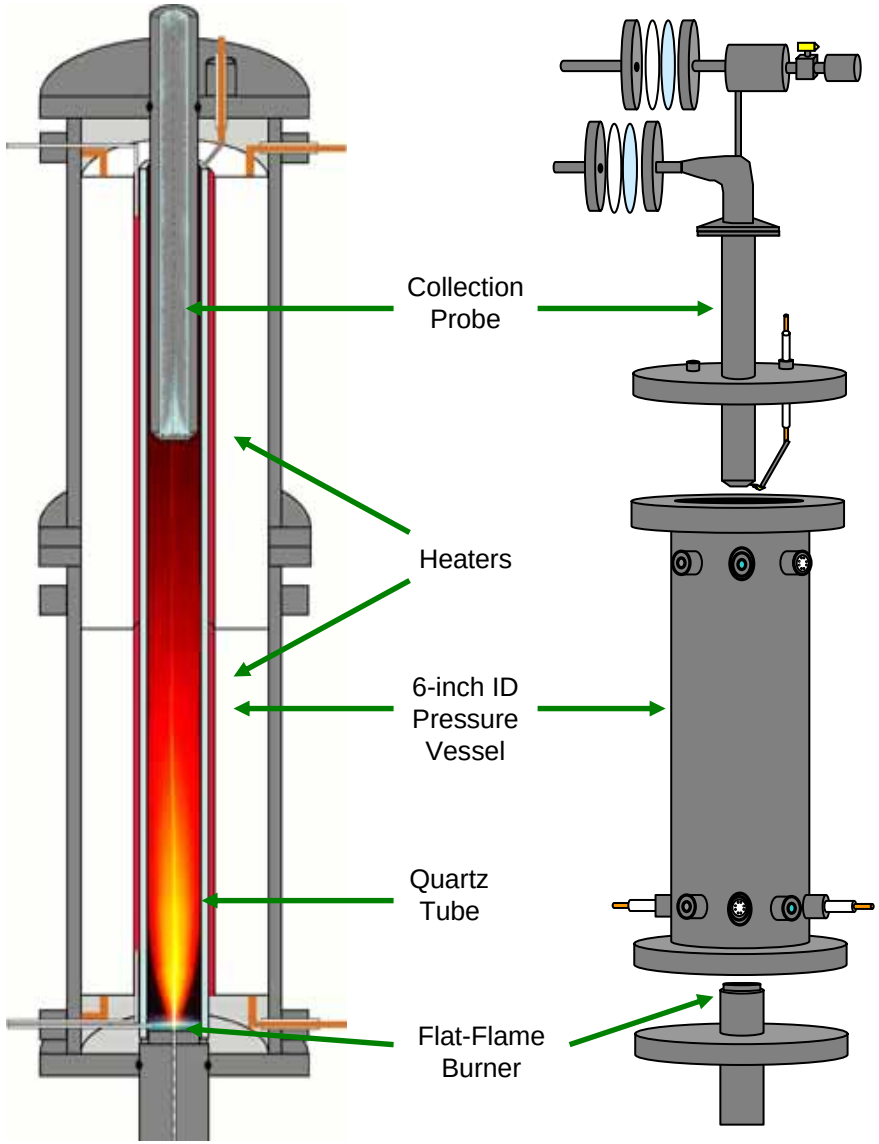
Atmospheric Flat-Flame Burner (FFB)

- Advantages:
  - Char and soot formation at high heating rate (~10^5 K/s)
  - Fueled by CH_4 or CO
    - Allows temperature flexibility (1100 K to 2000 K)
  - Adjust stoichiometry for $\%O_2$ in post-flame zone
  - Very fast heat-up and shut-down times for ease of use
  - Residence time adjusted easily
- Disadvantages:
  - Limited to experiments at ambient pressure

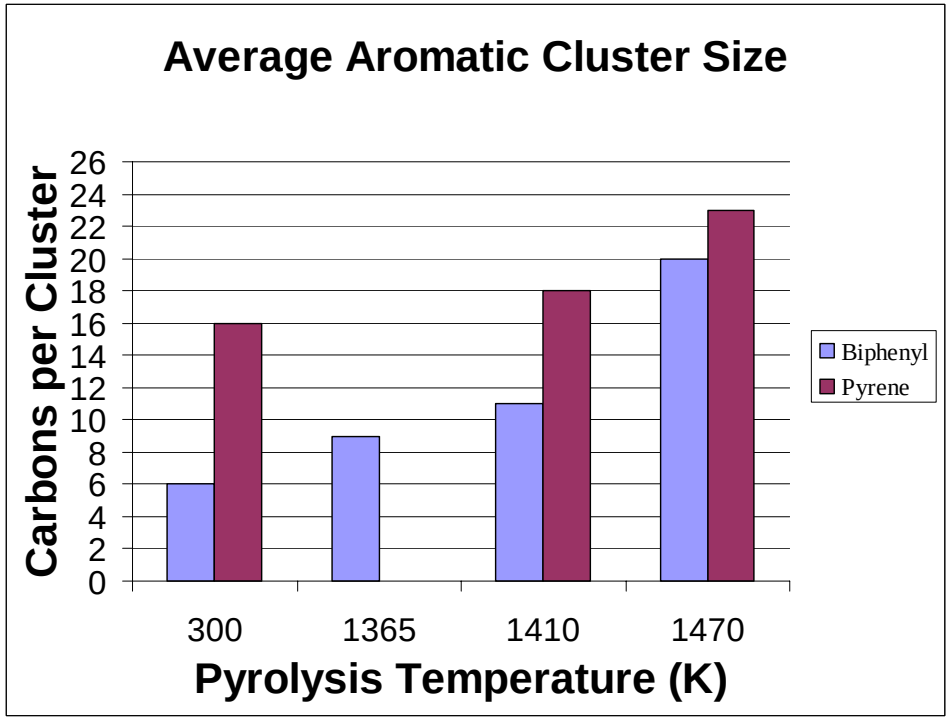


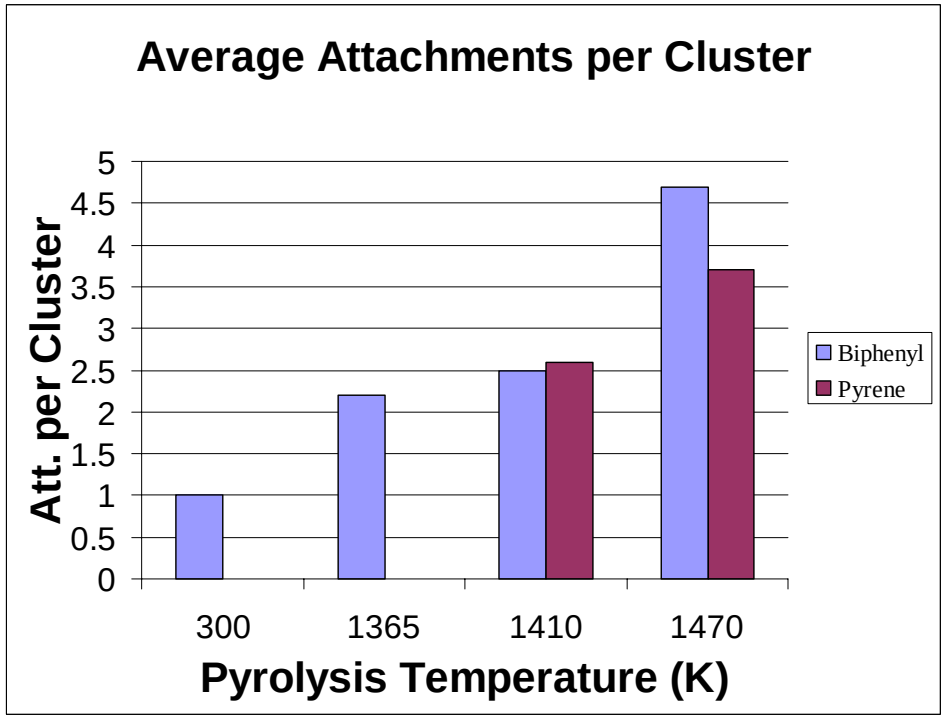
Pressurized Flat-Flame Burner (PFFB)

- Previous version retrofitted from a pressurized drop-tube reactor
  - Down-flow only
  - Movable burner and different quartz tubes to adjust residence time
  - Proven operation at 15 atm
- New Capabilities and Dimensions
  - Reduced pressure vessel ID to 6”
    - Combined heating/insulating units
  - Up-flow or down-flow
  - Probe moves to change residence time
    - 12-250 ms for 1 section
    - Up to 500 ms for 2 sections
    - Only 2 lengths of quartz tubing required
    - Simpler temperature profile measurement
  - Pressure vessel designed for 30 atm
    - Other required systems may limit operating pressure

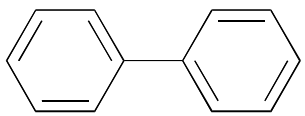


Average Structural Information Derived from NMR Data

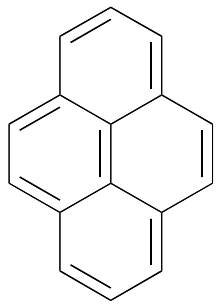




Biphenyl



Pyrene



Solum, Sarofim, Pugmire, Fletcher, Zhang, Energy & Fuels, **2001**, 15, 961-971.

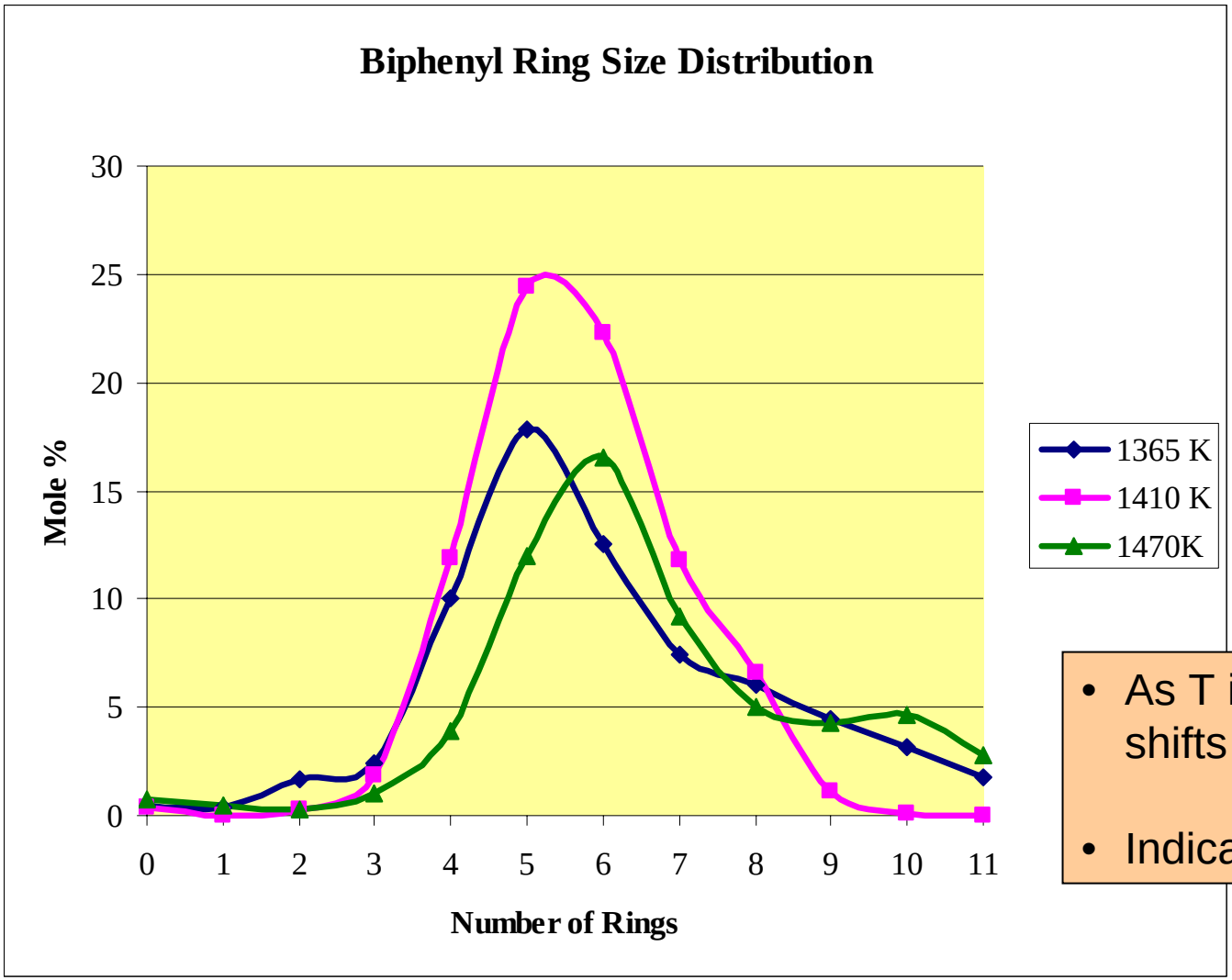
Unpaired Electron Spin Concentrations

Sample	N_e x 10^{19} spins/g
Biphenyl 1365 K	0.06
Biphenyl 1410 K	0.2
Biphenyl 1470 K	4.7
Pyrene 1410 K	2.0
Pyrene 1460 K	4.3

- This represents stabilized radical species
- Indicative perhaps of cluster size

Winans, Tomczyk, et. al., Energy & Fuels, 2007, 21, 2584-2593

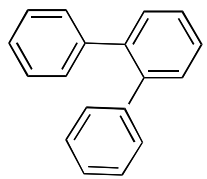
Distribution of Ring Sizes Determined by HRMS from Biphenyl Experiments



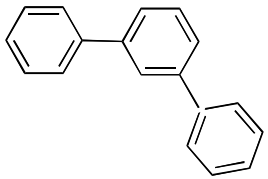
- As T increases, the peak shifts to higher ring number
- Indicative of cluster growth

Winans, Tomczyk, et. al., Energy & Fuels, 2007, 21, 2584-2593

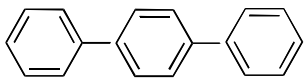
Distribution of *ortho*-, *meta*-, and *para*-terphenyl Structures from Biphenyl GCMS Data



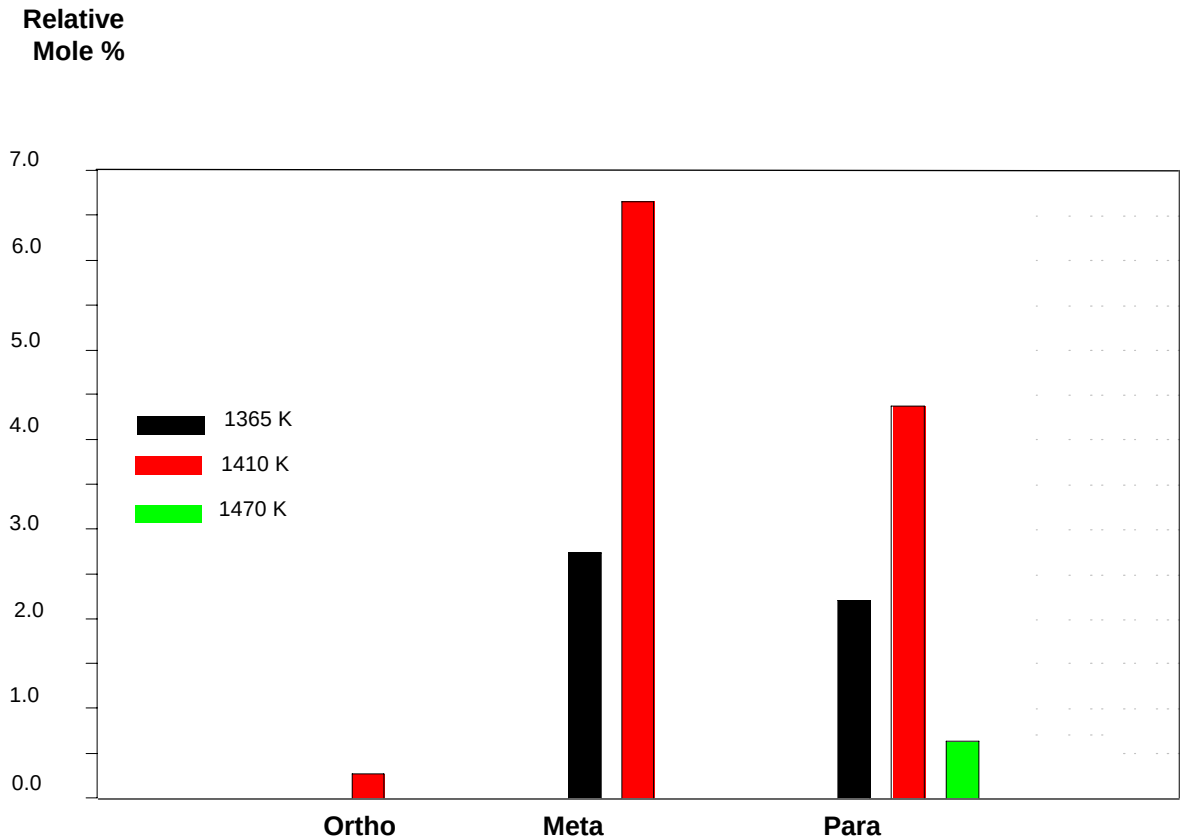
ortho-



meta-



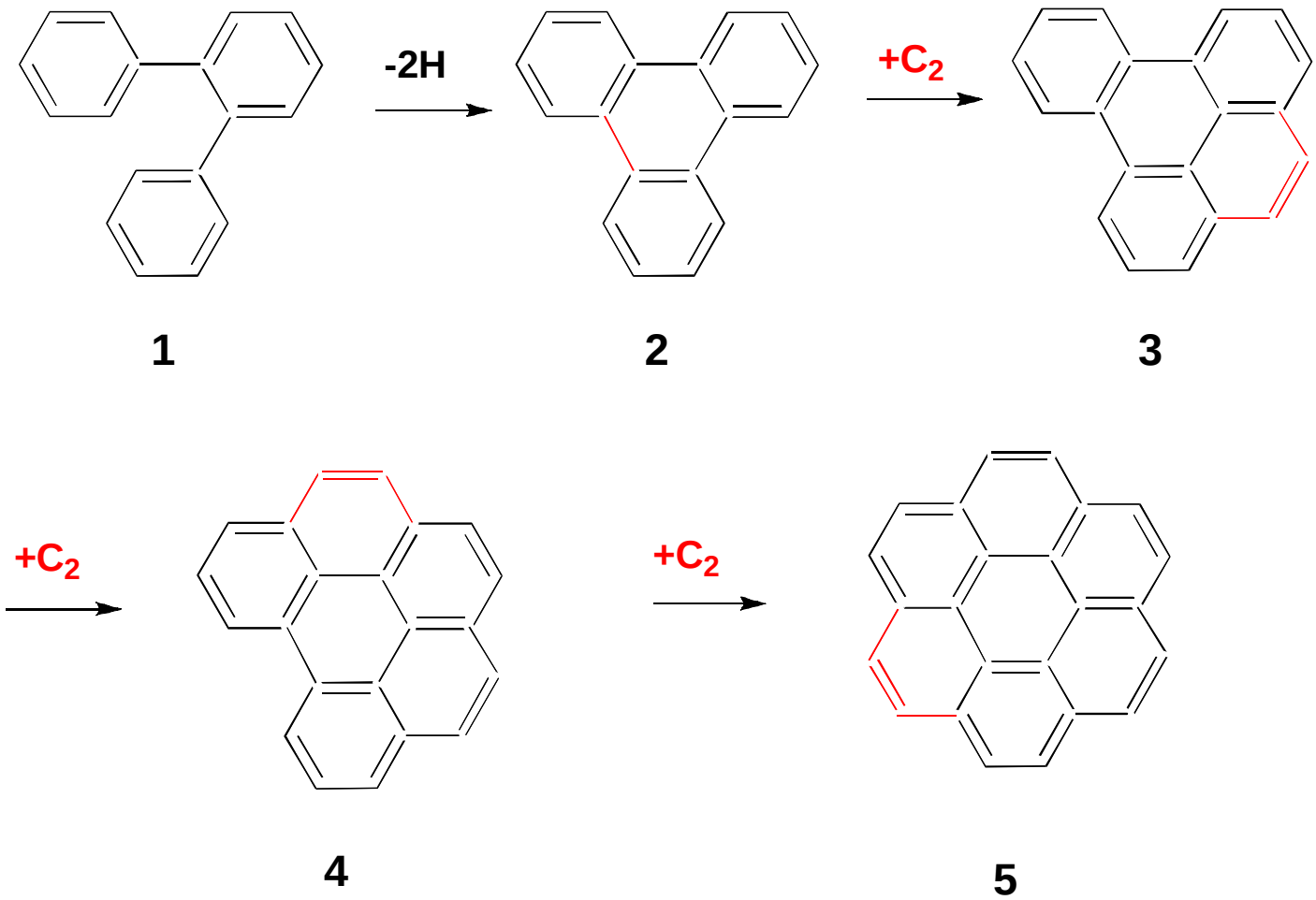
para-



Winans, Tomczyk, et. al., Energy & Fuels, 2007, 21, 2584-2593

- These compounds are formed from polymerization, not the HACA mechanism
- Many other compounds identified through GCMS, HRMS, and NMR

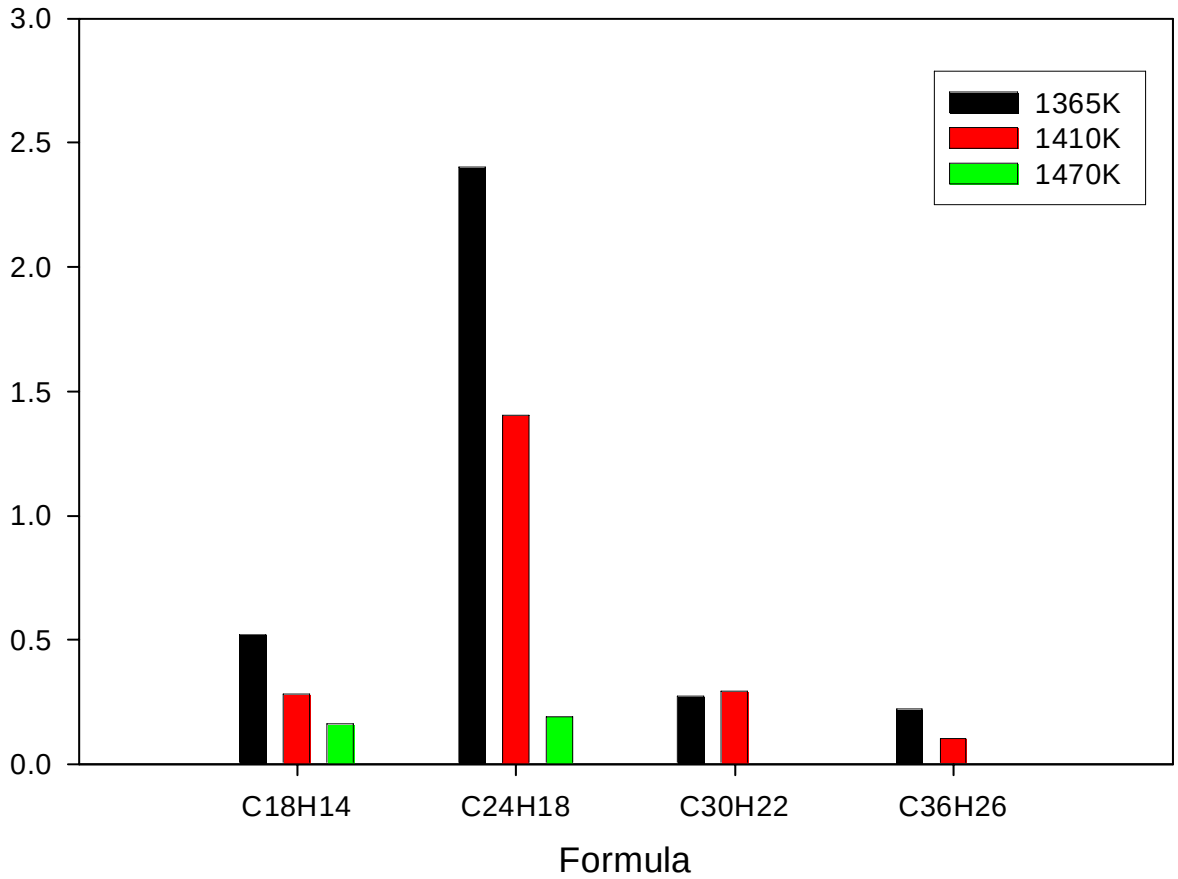
Examples of combination of polymerization and C_2H_2 Addition (Biphenyl mechanism)



Winans, Tomczyk, et. al., Energy & Fuels, 2007, 21, 2584-2593

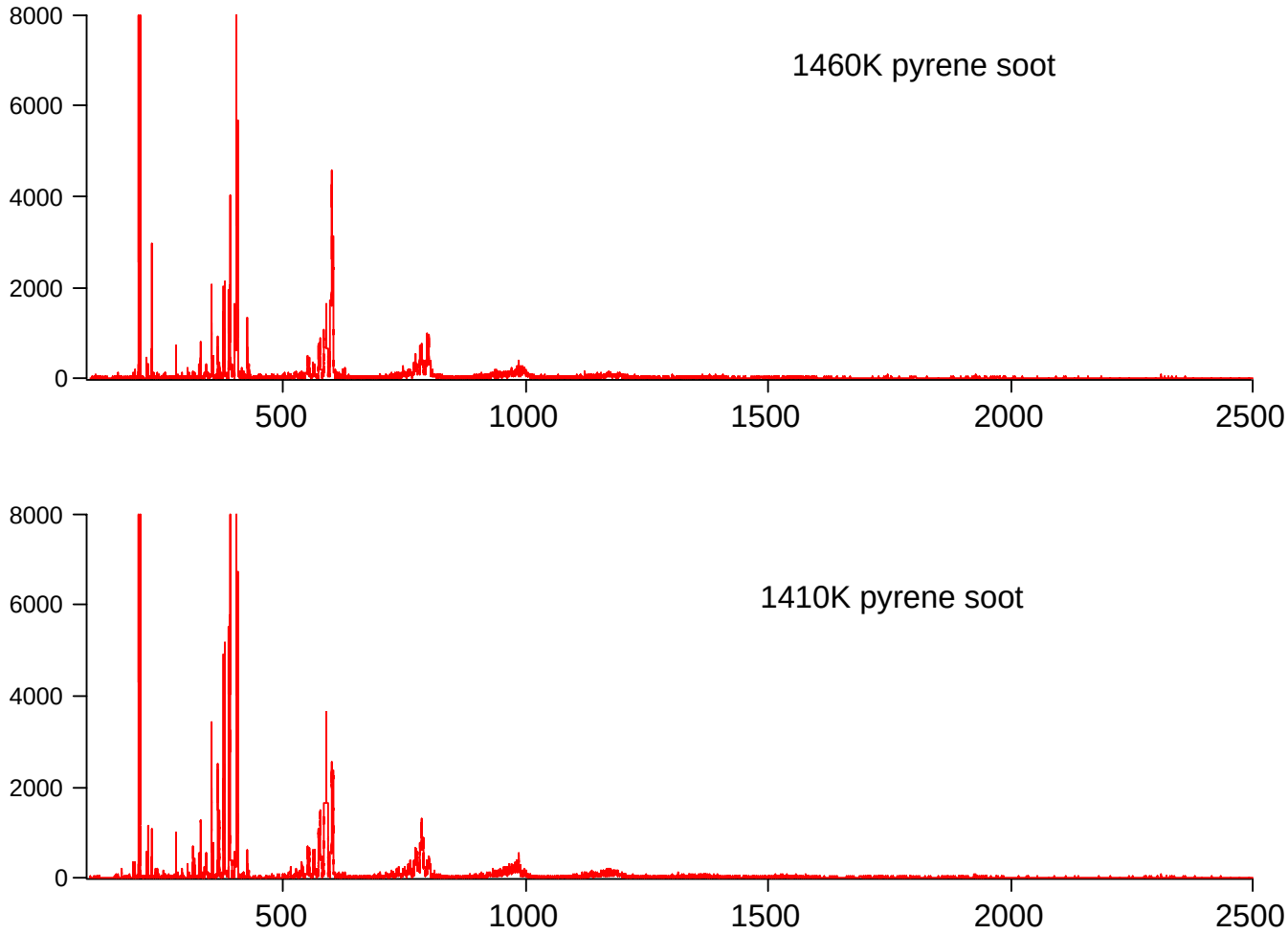
Relative Distributions of Polyphenyl Structures by HRMS From Biphenyl Experiments

Multiple polymers of biphenyl (C_{12}-C_{36}) provide many possible pathways to the complex PAH structures identified in soots



Winans, Tomczyk, et. al., Energy & Fuels, 2007, 21, 2584-2593

Laser Desorption Mass Spectra of Pyrene Soots at 1410 and 1460 K

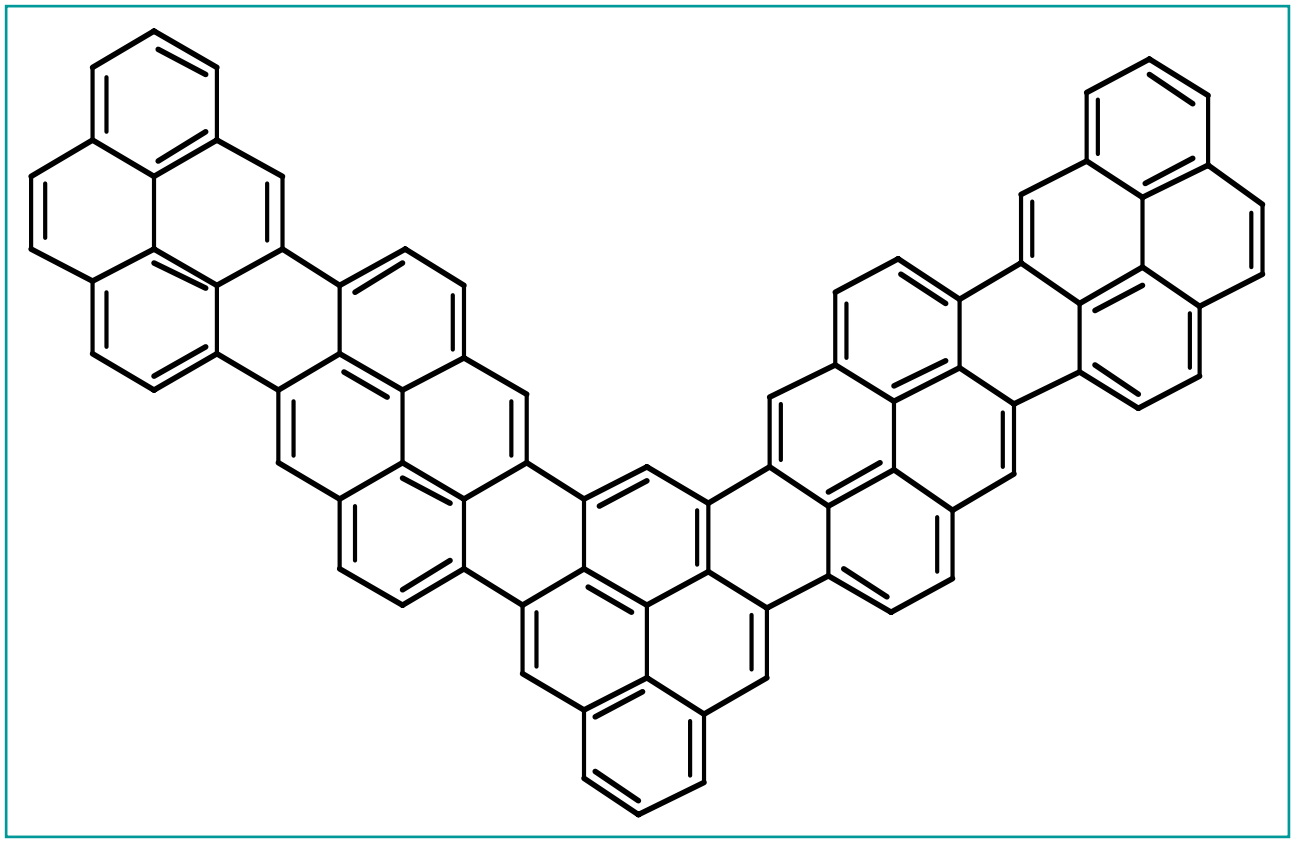


Winans, Tomczyk, et. al., Energy & Fuels, 2007, 21, 2584-2593

Schematic Structure of Pentamer of Pyrene Identified by LD-TOF

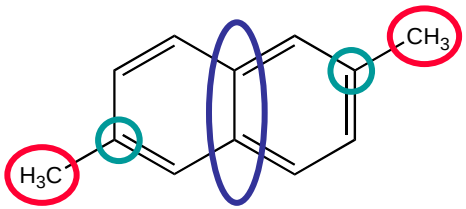
Corresponds to products of polymerization and dehyrogenation condensation products.

Polymerization creates molecular structures which are capable of undergoing dehydrogenative condensation to large graphite entities.



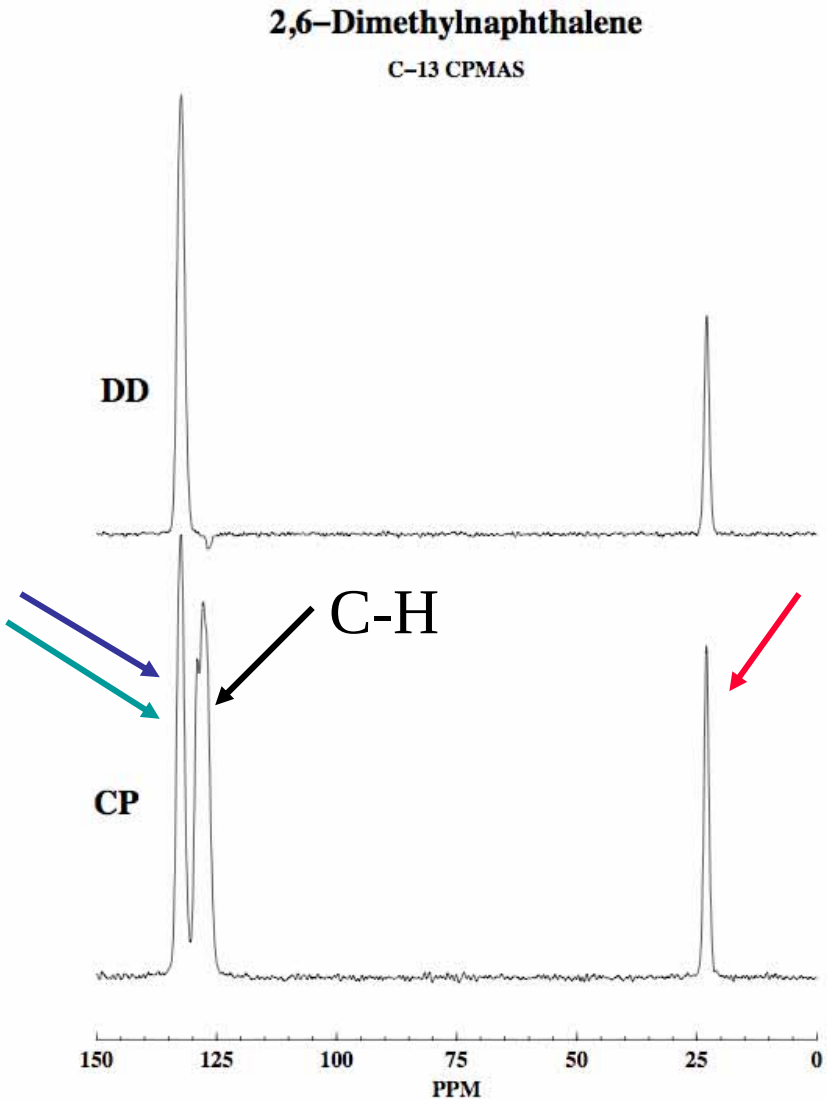
Winans, Tomczyk, et. al., Energy & Fuels, 2007, 21, 2584-2593

Current 13-C NMR Studies of 2,6-Dimethylnaphthalene



A. Dipolar Dephasing spectra

B. Cross polarization spectra



Structures Observed

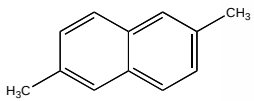
2,6-dmn

C = 10

σ + 1 = 2.0

S.C. = 2.0

f_{al} = 0.17

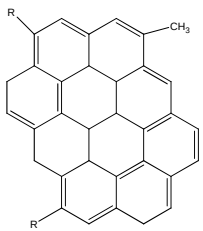


1447 K

C ~ 32

σ + 1 = 3.0

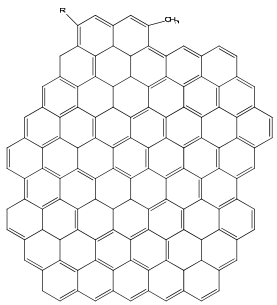
f_{al} = 0.04

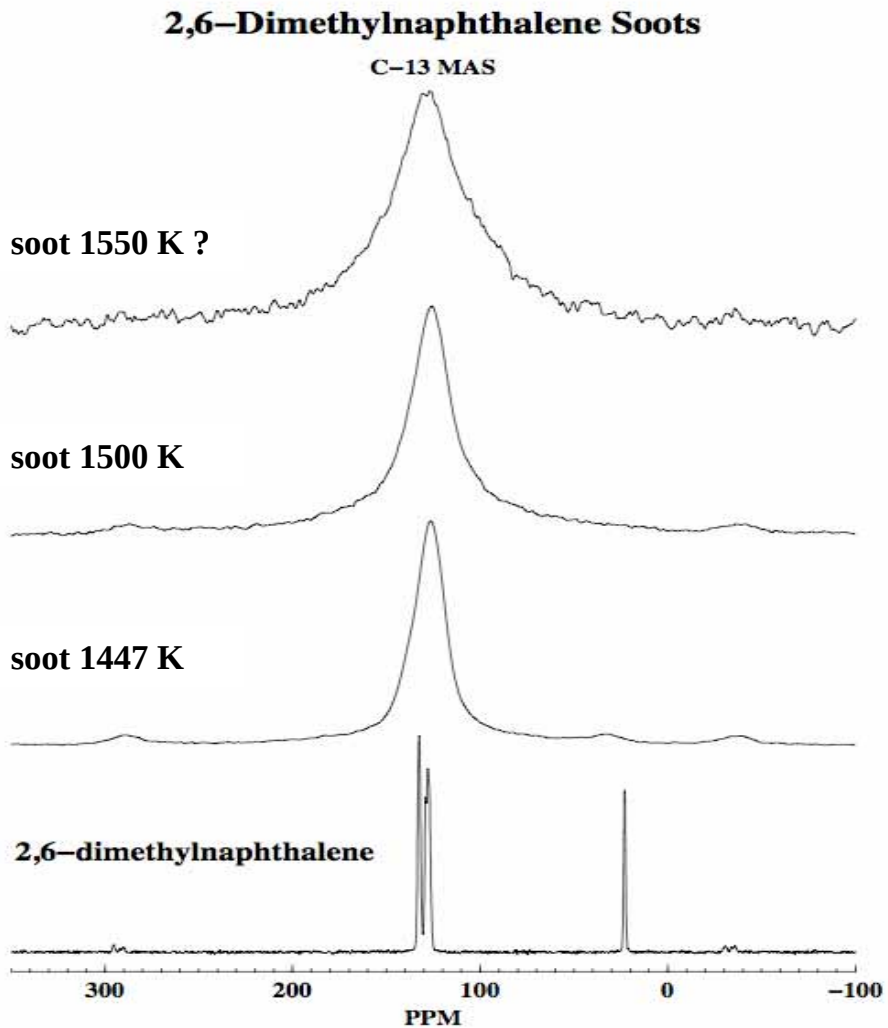


1500 K

C_{max} ~ 125

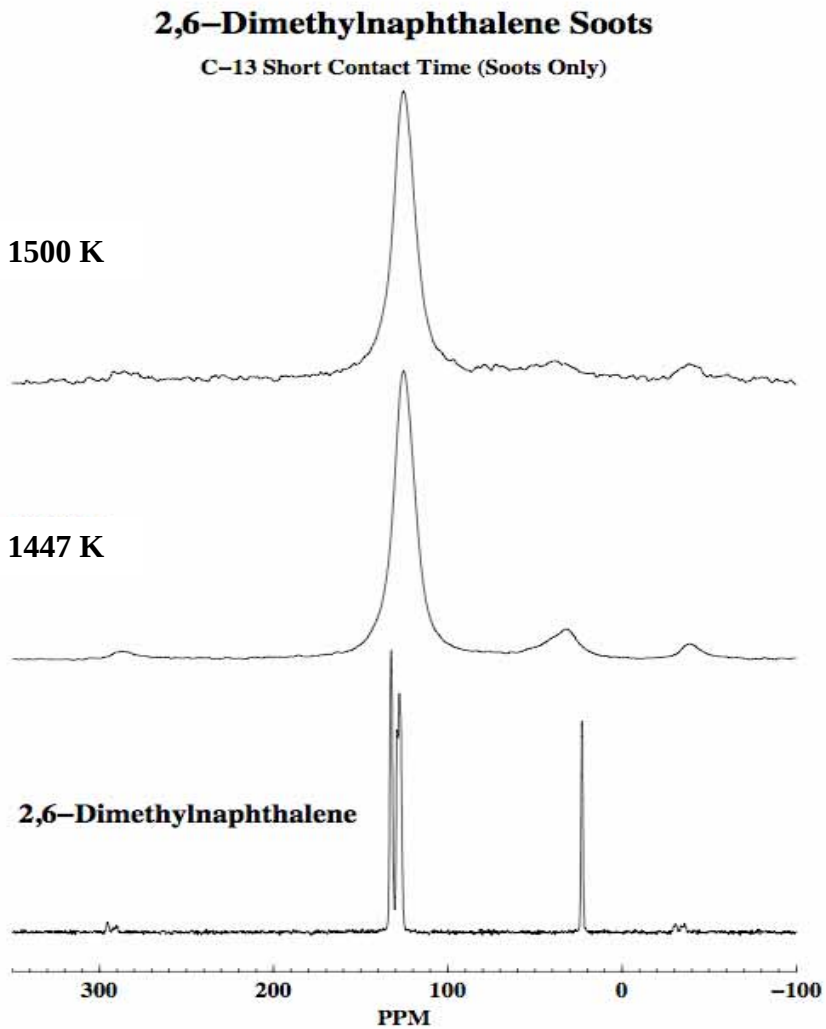
f_{al} ~ 0.02





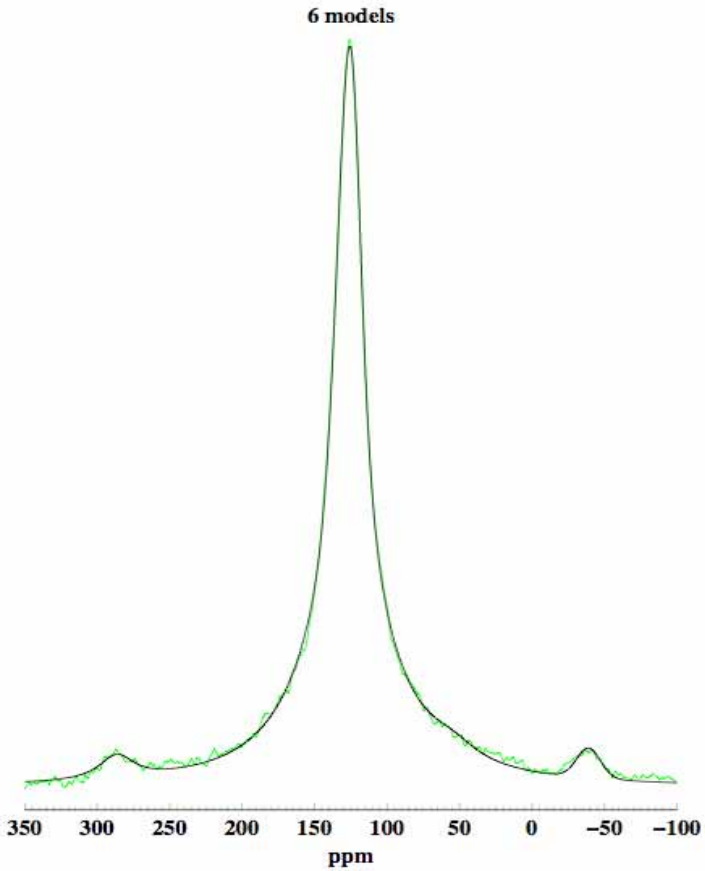
C-13 NMR Results

- By 1447 K essentially all of the methyl groups have disappeared
- At 1447 K new CH_2 and/or CH groups have formed
- At 1500 K these new aliphatic groups have largely disappeared.
- These spectra of soots only show protonated carbons.

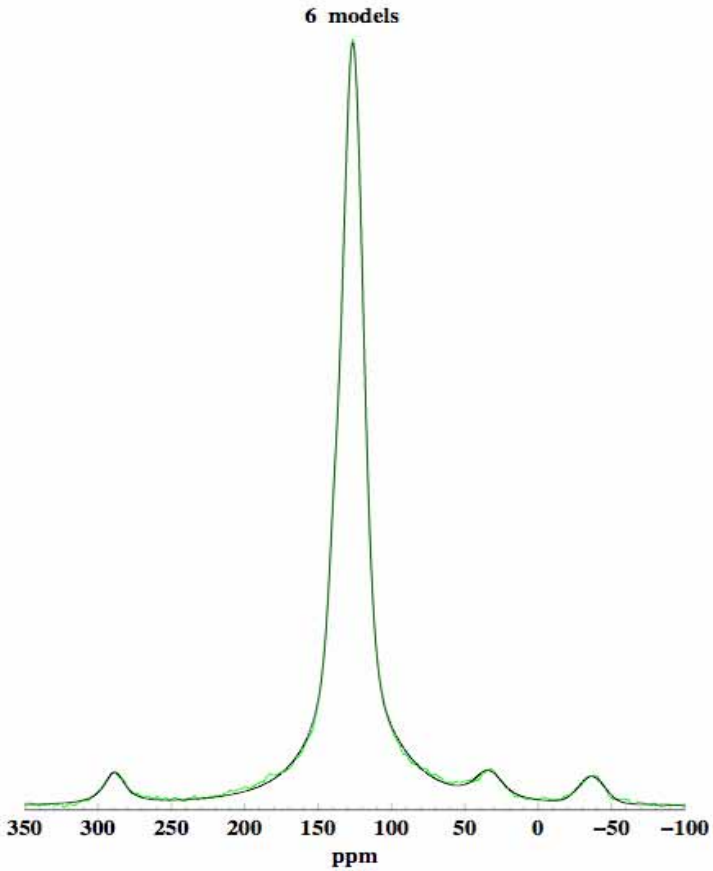


Influence of Temperature

2,6-Dimethylnaphthalene 1500 K Soot



2,6-Dimethylnaphthalene 1447 K Soot

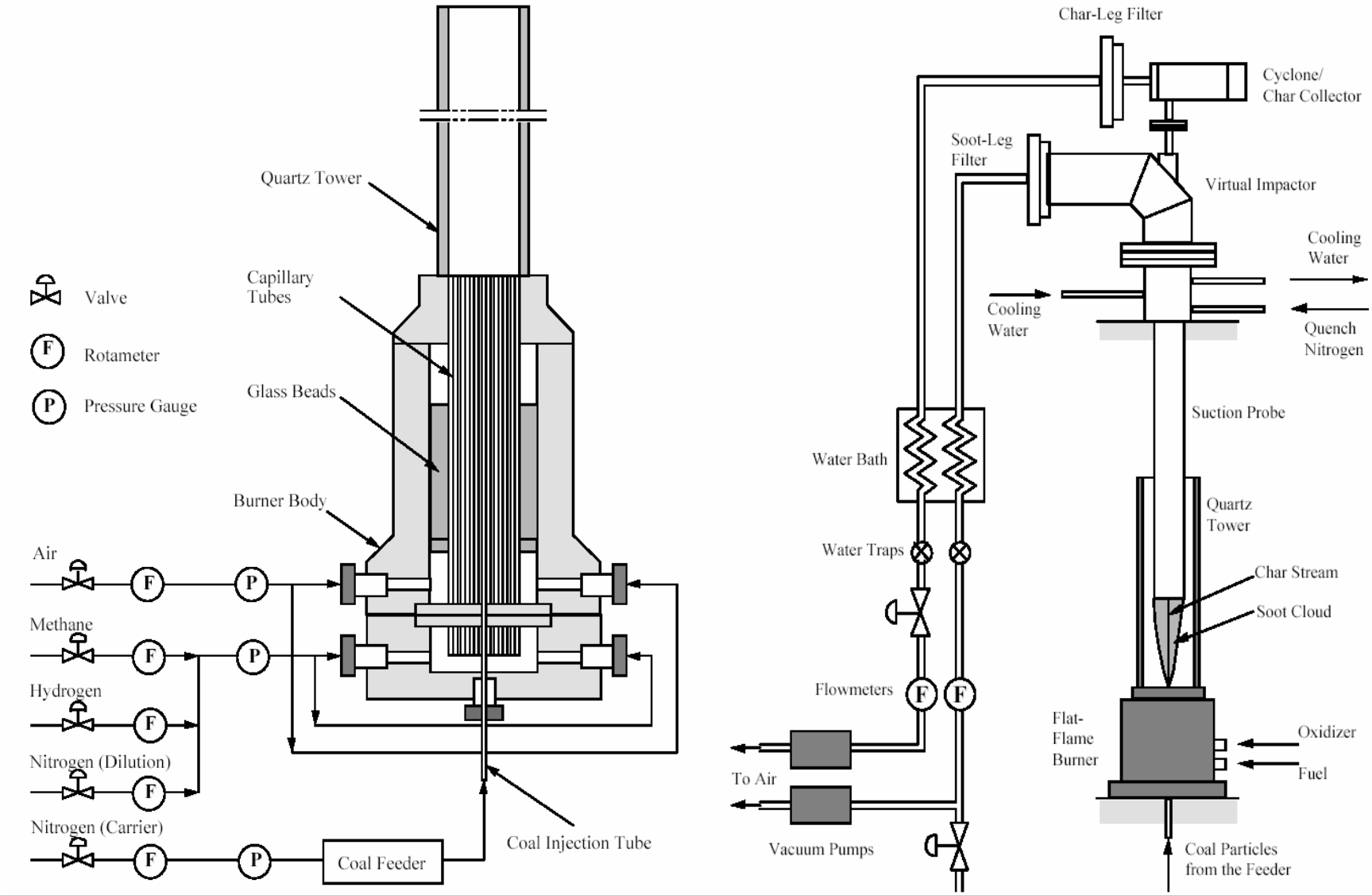


Conclusions

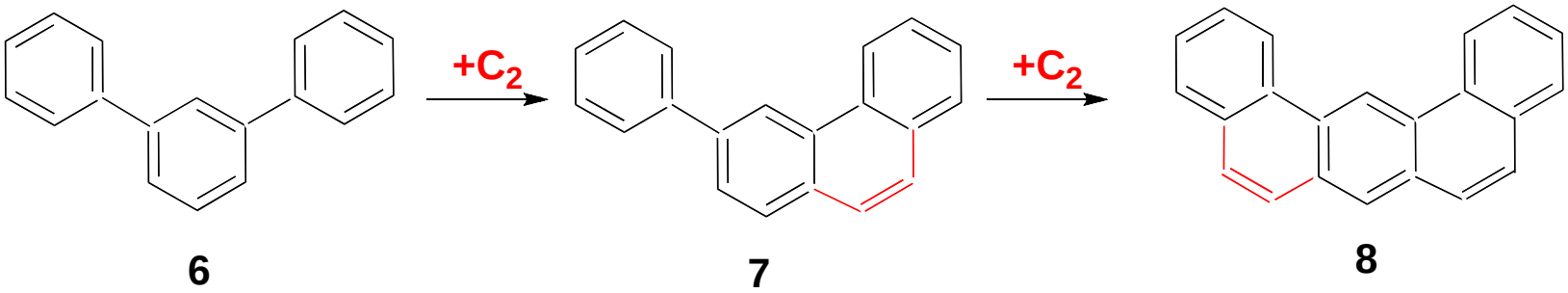
- **Coal tar does not simply consist of fused aromatic rings**
- **Contains aliphatic groups and O**
- **Simple model compounds were selected and analyzed**
- **NMR data provided the first clear evidence that polycondensation and polymerization reactions occur in the early stages of aerosol formation**
  - Different than the HACA mechanism
- **Free radical reactions are evident from ESR data**
- **Several hundred compounds were identified by GC-MS & HRMS.**
  - Structures ranging from biphenylene to $C_{42}H_{18}$ as well as the pentamer of pyrene
  - All structures identified can be rationalized by a combination of
    - polymerization
    - acetylene addition (i.e., HACA)

Thank You

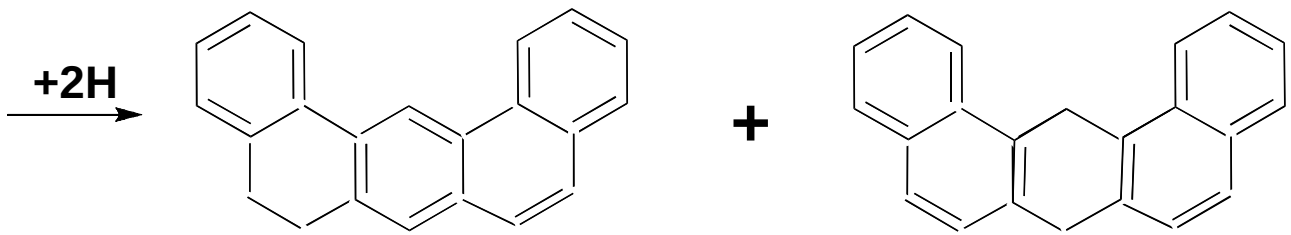
Atmospheric Flat-Flame Burner (FFB)



Examples of Possible Pathways from *m*-Terphenyl (Biphenyl mechanism)



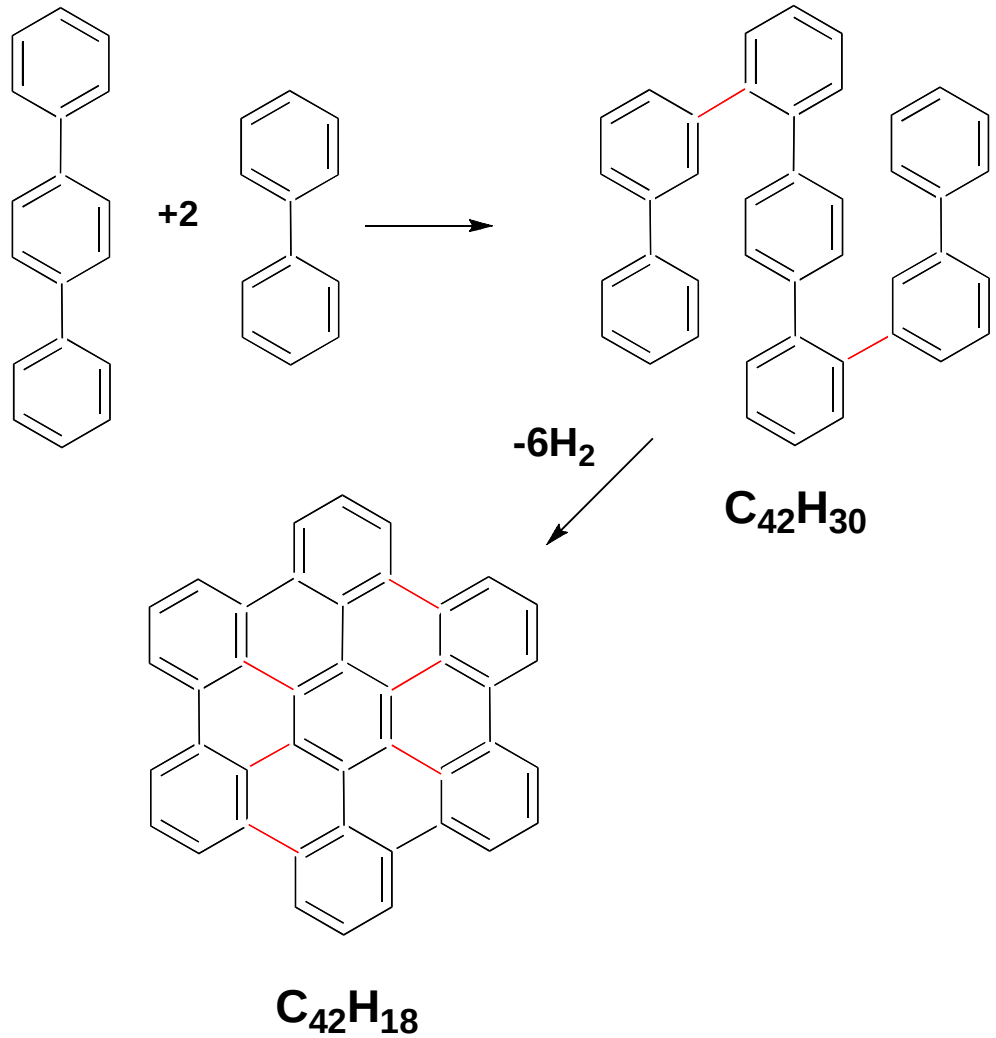
6 7 8



9 10

Schematic Pathway to Formation of “Star Dust” from Biphenyl

$C_{42}H_{18}$ has been Identified in intergalactic space and was identified in the biphenyl soot sample



Winans, Tomczyk, et. al., Energy & Fuels, 2007, 21, 2584-2593