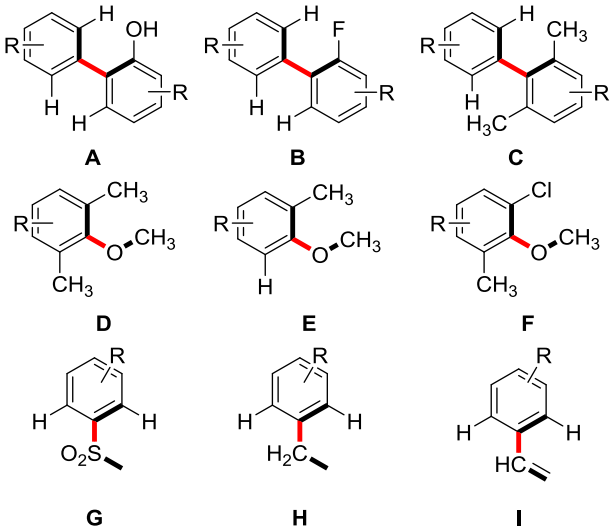
Problem Set 21.01.2014

1) Torsion Angles

Estimate the torsion angles of the following compounds. The central of the three bonds in bold was defined to be acyclic. Results are taken from a CSD search.

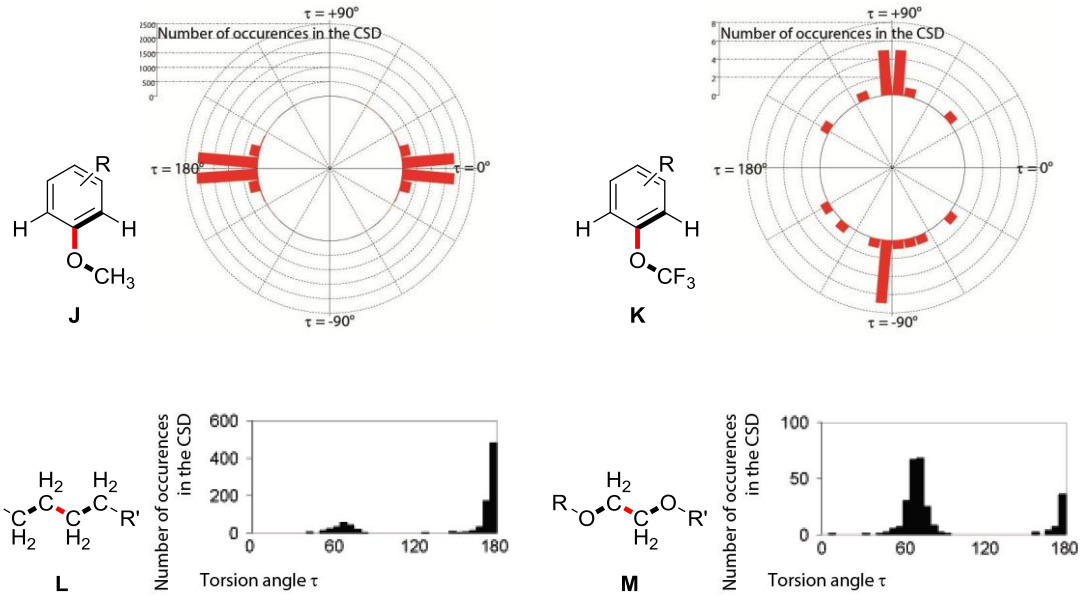
Hint 1: The solution for compound **J** in question 2 is for example 0 – 10°, *e.g.* the methoxy-substituent is in the same plane as the aromatic ring.

Hint 2: If it's not sterics, it's electronics.



2) Conformations

Please explain the different torsion angles τ observed in a CSD search for the pairs **J** and **K**, as well **L** and **M**.



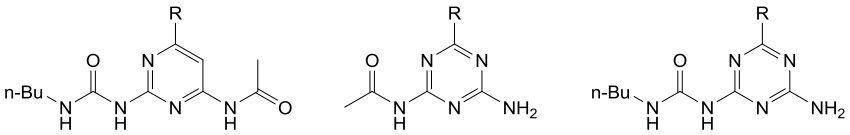
3) DNA base pairs

Draw the hydrogen bonds which stabilize the DNA (*e.g.* Watson-Crick base pairing). Melting points for double strand poly(AT) and poly(GC) were determined as 50.9 °C and 103.8°C. Assign the respective melting points.

4) Hydrogen bond networks

Compounds **N**–**P** form homodimers. Draw the most stable homodimers (**N·N, O·O, P·P**). Dimerization constants K of 530 M^{-1}, $2x10^4$ M^{-1}, and $2x10^5$ M^{-1} were measured in $CDCl_3$. Assign these values to the respective complexes and explain your choice. Calculate the corresponding Gibbs free energies ($-\Delta G$) for complex formation at room temperature.

Hint: NMR studies confirmed that the tautomers drawn below are present in solution.



N **O** **P**

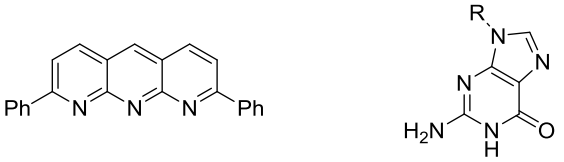
Bonus question: what is the range (Å) for O/N–H···O/N hydrogen bonds?

5) Hydrogen bond patterns

Use compounds **Q**–**V** to form three pairs of heterodimers (use each compound once only). Assign the equilibrium constants measured in $CDCl_3$ (K = 90 M^{-1}, 10^4 M^{-1}, $\geq 10^5$ M^{-1}) to each heterodimer.

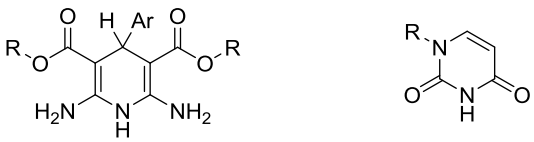
Hint 1: A simplified model using D for H-bond donor and A for H-bond acceptor could help, look out for secondary interactions.

Hint 2: The tautomers drawn are the ones present in solution.



Q **R**

S **T**



U **V**