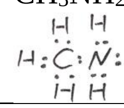
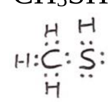
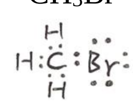
Carnegie Mellon University
Department of Civil and Environmental Engineering

12-725: Fate, Transport, and Physicochemical Processes of Organic Contaminants in Aquatic Systems and their Measurement in Environmental Samples

Spring 2020 Problem Set #1-<u>solutions</u>
Due January 23, 2019 (in folder in front of my office by 5pm or uploaded to Canvas)

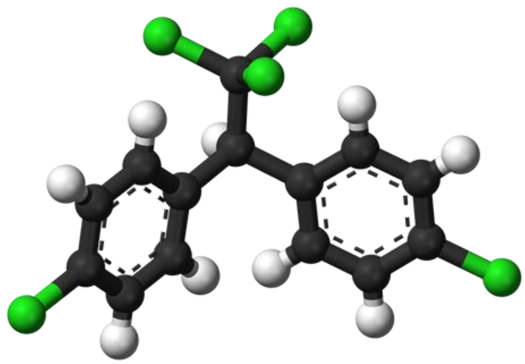
1. How many valence electrons are there in C, N, S, and Br? How many bonds must each atom have in an organic molecule to fill the outer valence shell? Give three example organic molecules containing the following heteroatoms (i.e. one molecule with N, one with O, and one with S) showing the *Lewis Structure* for each. Label each electron in the structure with a dot. Make sure that the total number of valence electrons in your structure match expectations.

	C	N	S	Br
Valence Electrons	4	5	6	7
Bonds	4	3	2 or 6	1
Organic compound	/	CH_3NH_2	CH_3SH	CH_3Br
Lewis structure	/			

2. Q 2.4 in your textbook (EOC). **NOTE: There are QUESTIONS (labeled Q) and PROBLEMS (Labeled P) in your book. *They are different.* Be sure to look at the QUESTIONS here.**

   The structure of a given compound describes the architecture, spatial arrangements and chemical composition of a given compound. Architecture and spatial arrangements describe the type of chemical bonds connecting atoms and the bond angles. Chemical compositions describe the elements forming a given compound.
   Structural isomers are compounds with the same molecular formula (chemical composition) but different chemical bonding arrangements including different orders and chemical bond types.

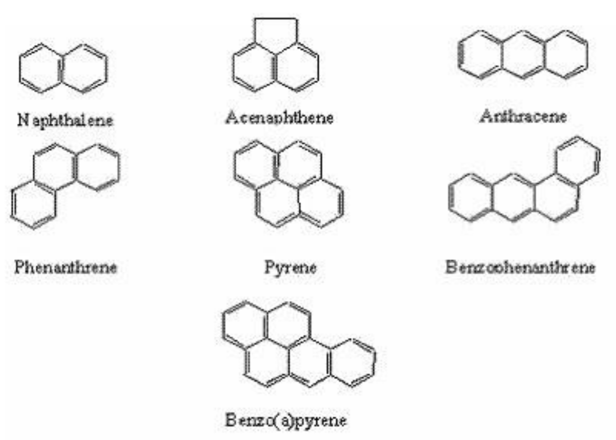
3. Give the *approximate* bond angle for all of the <u>carbon atoms</u> in DDT shown below? How many "different" carbon atoms are there with respect to their approximate bond angels? How many different carbon atoms are there with respect to their local bonding environment, i.e. with respect to the other atoms around them?

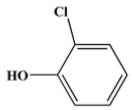


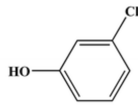
The carbons in ring structures are SP2 hybridized and are approximately 120°. The other two carbons are tetrahedral (SP3 hybridized) so they are closer to 109.5°. Note that the three chlorine atoms on the methyl group would likely repel one another and therefore the Cl-C-C bond angle is a little bit LESS than 109.5°. Similarly, the two phenyl groups attached to the central carbon would likely push apart a bit, making the phenyl-C-phenyl bond slightly greater than 109.5°. Thus, the bond angles in the rings are all essentially the same (1), the central C atoms (2) is different than the methyl group (3). This leads to ~3 types of C atoms with respect to bond angle. For the bonding environment, clearly the methyl group and the central C atom are different because they have different bonded constituents. The phenyl groups are identical, but there are four different types of C atoms in them: 1-the C attached to the central C atom, 2-the next two C atoms in the rings, 3-the next 2 C atoms in the rings (closer to the Cl atom), and 4-the C atom attached to the Cl atom.

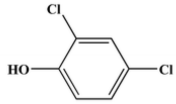
4. Give the IUPAC names and draw the corresponding structure of a compound in each of these compound classes: (i) Polyaromatic hydrocarbons (ii) chlorophenols, (iii) amines, (iv) organohalides, (v) perfluorinated alkane sulfonates.

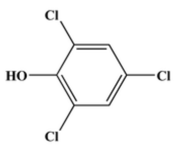
i)

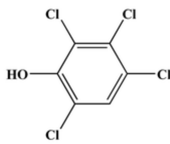


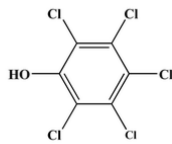

2-chlorophenol
pKa = 8.55


3-chlorophenol
pKa = 9.12

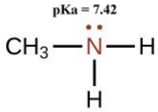

2,4-dichlorophenol
pKa = 7.85

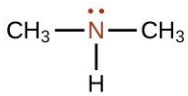

2,4,6-trichlorophenol
pKa = 7.42

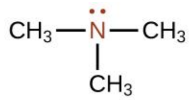

2,3,4,6-tetrachlorophenol
pKa = 5.62


pentachlorophenol
pKa = 4.74

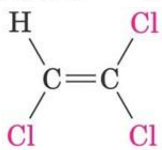
ii)

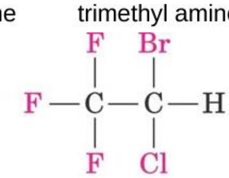

methyl amine

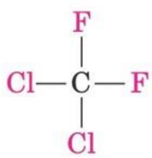

dimethyl amine

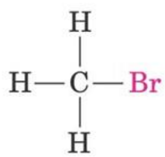

trimethyl amine

iii)

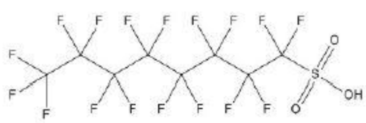

Trichloroethylene
(a solvent)

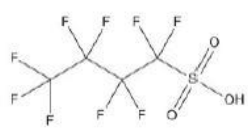

Halothane
(an inhaled anesthetic)

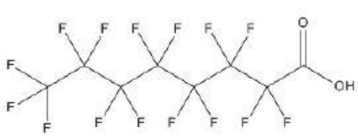

Dichlorodifluoromethane
(a refrigerant)


Bromomethane
(a fumigant)

iv)


Perfluorooctane sulfonic acid (PFOS)


Perfluorobutane sulfonic acid (PFBS)


Perfluorooctanoic acid (PFOA)

v)

5. Explain the terms apolar, bipolar, and monopolar as they apply to organic compounds. Give one example of each type of compound.

   Apolar: These compounds undergo only van der Wall interactions. The center of the positive charge is in the same location of the center of the negative charge. e.g. CH_4, hydrocarbons, PCBs, and chlorinated benzenes.
   Monopolar: These compounds are either electron donors (ED) or electron acceptors (EA), but not both. These arise because the center of the positive charge is not in the same location of the center of the negative charge so there is dipole inside the molecule: e.g. CH_3CO, C=O, R-C-O-C-R.
   Bipolar: These compounds that contain O-H or N-H, or an F-H bond that have both an electron donor and an electron acceptor. Importantly, these compounds can form hydrogen bonds with itself: e.g. CH_3CH_2OH, R-NH_3.

6. What types of intermolecular interactions may occur for pure liquids or gases of ethanol, ethoxyethane, H_2S, and ethylamine? What types of interactions may occur for these molecules when dissolved in water?

   In pure liquids and gas:
   1. The major intermolecular force for ethanol is H-bonding as it is a bipolar compound, it can also form dipole-dipole forces, dipole-induced dipole forces and dispersive forces.
   2. Ethoxyethane is a monopolar compound. It can form dipole-dipole forces, dipole-induced dipole forces and dispersive forces in pure phase.
   3. H_2S is also a monopolar compound. Can mainly form dipole-dipole forces. Dipole-induced dipole forces and dispersive forces can also form in pure phase. Note that it was recently reported that H2S does form dimers (i.e. H-bonding) at low temepratures (A Das *et al*, *Angew. Chem., Int. Ed.*, 2018, DOI: 10.1002/anie.201808162)
   4. Ethylamine is a bipolar compound. The major intermolecular force is H-bonding. It can also form dipole-dipole forces, dipole-induced dipole forces and dispersive forces.

   When dissolved in water:
   1. The major intermolecular force for ethanol and water is H-bonding. Dipole-dipole forces, dipole-induced dipole forces and dispersive forces can also form.
   2. Ethoxyethane can form hydrogen bonds with water. It can also form dipole-dipole forces, dipole-induced dipole forces and dispersive forces either with water or with itself.
   3. H_2S can form dipole-dipole forces, dipole-induced dipole forces and dispersive forces with water and with itself.
   4. Ethylamine can form H-bonding, dipole-dipole forces, dipole-induced dipole forces and dispersive force with itself and with water.

7. H-bonding in water is about 20 kJ/mol, and is stronger than for HF. Hydrogen bonding in HF is stronger than for NH_3. Give a reasonable explanation for why hydrogen bonding for water molecules is highest, and why HF is higher than for NH_3?

The H-bonding depends on both the electron negativity of the electron rich sites (O, N, F) and number of H-bonding that could form between molecules. Although fluorine in HF is more electron negative than oxygen in water, HF could only form one H-bond with each other, while water can form two H-bond with each other. This makes H-bonding in water stronger than HF. NH_3 also only forms one H-bond per molecule. Also, N is not as electron negative as F, which makes the attraction weaker. So, the H-bonding between NH_3 is weaker than HF.

8. Define a "functional group" on a molecule. Give three examples of functional groups and a brief explanation of what that group does to the properties of organic molecules.

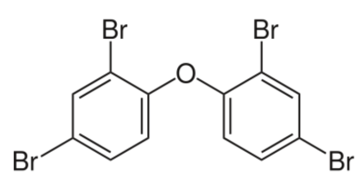
Functional groups are a specific combination of atoms that are responsible for the characteristic chemical interaction and reactions of a molecule. The same functional groups on different molecules should bring similar chemical properties to those compounds.
Hydroxyl group, -OH: Makes the compound able to H-bond and to be more hydrophilic, e.g. can dissolve more in water.

Carboxylic acid: Makes the compound more hydrophilic compared to the -OH group. The COOH group can dissociate at higher pH (above the pKa), resulting in a charged molecule. It also brings acidity to the compound.

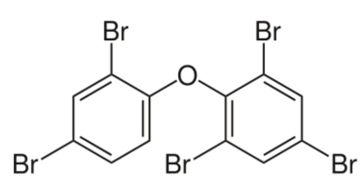
Halogen: e.g. -Cl, -F. They introduce EN bonds, but in general these tend to make compounds more hydrophobic due to the large size of the C or F compared to H. We will discuss this more later in the course. The halogen also tend to increase toxicity and persistence of the compounds compared to those without halogens.

9. The EPA assessed the bioaccumulation a class of flame retardants known as polybrominated diphenylethers (PBDE). BDE-47 and BDE-100 are typically found in the greatest concentrations. Give the IUPAC name and structure for BDE-47 and BDE-100. Why is the EPA concerned about these chemicals?

IUPAC name of BDE-47: 2,2',4,4'-Tetrabromodiphenyl ether
Structure of the compound:

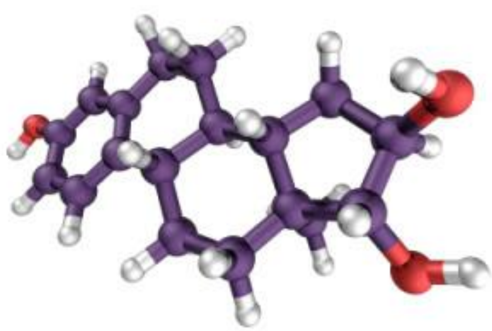


IUPAC name of BDE-100: 2,2′,4,4′,6-penta-bromodiphenyl ether
Structure of the compound:



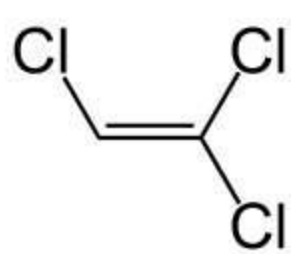
EPA is concerned that certain PBDE congeners are persistent, bioaccumulative, and toxic to both humans and the environment. The critical endpoint of concern for human health is neurobehavioral effects. Various PBDEs have also been studied for ecotoxicity in mammals, birds, fish, and invertebrates. In some cases, current levels of exposure for wildlife may be at or near adverse effect levels.
PBDEs are not chemically bound to plastics, foam, fabrics, or other products in which they are used, making them more likely to leach out of these products. Despite the United States having phased out the manufacture and import of penta- and octaBDE in 2004, their component congeners are being detected in humans and the environment. Some reports indicate that levels are increasing. One potential source is imported articles to which these compounds have been added. Another is the possible breakdown of decaBDE in the environment to more toxic and bioaccumulative PBDE congeners.
EPA has concerns with decaBDE's hazards as well as its potential to be transformed to other PBDE congeners. DecaBDE was included in EPA's Voluntary Children's Chemical Evaluation Program (VCCEP), which identified a number of tests needed to better understand decaBDE's potential for transformation.

10. Determine the average oxidation state of carbon and/or nitrogen in each of the following compounds:



The compound is Estriol. Chemical formula is: $C_{18}H_{24}O_3$. The average oxidation state of carbon is:

$$AOSc = \frac{(+1 \times 3) - 1 \times 24}{18} = -1.17$$



The compound is trichloroethene. Chemical formula is: C_2HCl_3. Average oxidation state of carbon is:

$$AOSc = \frac{(+1 \times 3) - 1}{2} = 1$$

12725 HW1 Rubrics

Problem 4 (20):

5 correct drawings, each is 4 points

Problem 5 (20)

Apolar (6):

- only Van der Wall interaction
- positive charge in the same location of the center of the negative charge
- examples

Monopolar (6):

- either ED or EA
- the center of the positive charge is not in the same location of the center of the negative charge and there is dipole inside
- examples

Bipolar (8):

- contain O-H, or N-H or an F-H bond
- both ED and EA
- can form hydrogen bond
- examples

Problem 8 (20)

Definition of functional group (5):

- a specific combination of atoms
- responsible for characteristic chemical and reactions of a molecule
- same functional groups → similar chemical properties

3 examples of functional groups with clear explanations on what chemical characteristics the group brings to the compound. Each is assigned with 5 points

e.g. Carboxylic acid

- more hydrophilic
- dissociate at higher pH and result in a charged molecule
- brings acidity