CH 233H

Second Midterm Exam

Friday, May 13, 2016

Name____KEY_____

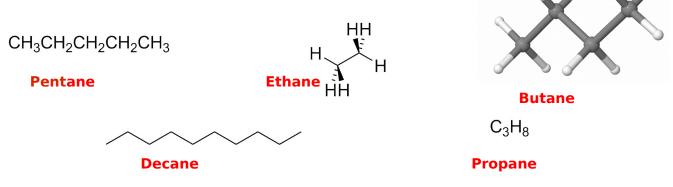
Please show your work for partial credit. If you need more space for an answer, use the back of the page and indicate where we should look.

You may not use notes or other materials with chemical information without the instructor's approval; necessary information is provided on pages at the back of the exam. Please do not use ipods or other music players.

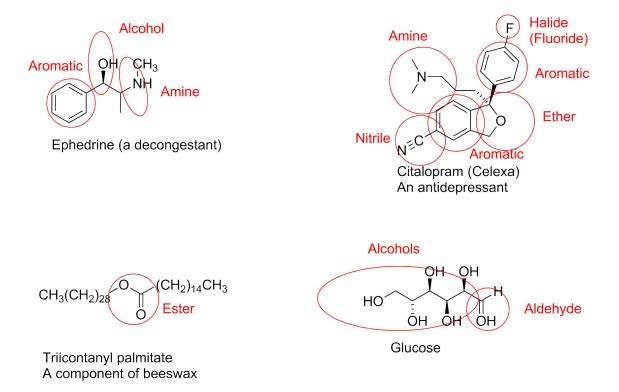
hydrogen 4	1 100																1945 - S	helium 2
Ĥ																		Н́е
1.0079 lithium	beryllium												boron	carbon	nitrogen	oxygen	fluorine	4.0026 neon
3	4												5	6	7	8	9	10
Li	Be												B	С	N	0	F	Ne
6.941	9.0122												10.811	12.011	14.007	15.999	18.998	20.180
sodium 11	magnesium 12												aluminium 13	silicon 14	phosphorus 15	sulfur 16	chlorine 17	argon 18
														Si	P	S	10.0	1000
Na	Mg												ΑΙ		market Commission		CI	Ar
22.990 potassium	24.305 calcium		scandium	titanium	vanadium	chromium	manganese	iron	cobalt	nickel	copper	zinc	26.982 gallium	28.086 germanium	30.974 arsenic	32.065 selenium	35.453 bromine	39.948 krypton
19	20		21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36
K	Ca		Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
39.098	40.078		44.956	47.867	50.942	51,996	54,938	55.845	58,933	58,693	63,546	65.39	69.723	72.61	74,922	78.96	79.904	83.80
rubidium	strontium		yttrium	zirconium	niobium	molybdenum	technetium	ruthenium	rhodium	palladium	silver	cadmium	indium	tin	antimony	tellurium	iodine	xenon
37	38		39	40	41	42	43	_44	45	46	47	48	49	50	51	52	53	54
Rb	Sr		Y	Zr	Nb	Mo	TC	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Те		Xe
85.468	87.62		88.906	91.224	92.906	95.94	[98]	101.07	102.91	106.42	107.87	112.41	114.82	118.71	121.76	127.60	126.90	131.29
caesium 55	barium 56	57-70	lutetium 71	hafnium 72	tantalum 73	tungsten 74	rhenium 75	osmium 76	iridium 77	platinum 78	gold 79	mercury 80	thallium 81	lead 82	bismuth 83	polonium 84	astatine 85	radon 86
126.0563	2224224					1. S.	122624		1000				TI					
Cs	Ba	*	Lu	Hf	Та	W	Re	Os	Ir	Pt	Au	Hg	11	Pb	Bi	Po	At	Rn
132.91 francium	137.33 radium		174.97 lawrencium	178.49 rutherfordium	180.95 dubnium	183.84 seaborgium	186.21 bohrium	190.23 hassium	192.22 meitnerium	195.08 ununnilium	196.97 unununium	200.59 ununbium	204.38	207.2 ununquadium	208.98	[209]	[210]	[222]
87	88	89-102	103	104	105	106	107	108	109	110	111	112		114				
Fr	Ra	* *	0,000,000	Rf	Db		Bh	Hs	Mt		Uuu			Uuq				
			Lr			Sg												
[223]	[226]		[262]	[261]	[262]	[266]	[264]	[269]	[268]	[271]	[272]	[277]		[289]				

*Lanthanide series	lanthanum 57	cerium 58	praseodymium 59	neodymium 60	promethium 61	samarium 62	europium 63	gadolinium 64	terbium 65	dysprosium 66	holmium 67	erbium 68	thulium 69	ytterbium 70
Lanthanide Series	La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb
	138.91	140.12	140.91	144.24	[145]	150.36	151.96	157.25	158.93	162.50	164.93	167.26	168.93	173.04
	actinium	thorium	protactinium	uranium	neptunium	plutonium	americium	curium	berkelium	californium	einsteinium	fermium	mendelevium	nobelium
* * Actinide series	89	90	91	92	93	94	95	96	97	98	99	100	101	102
	Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No
	[227]	232.04	231.04	238.03	[237]	[244]	[243]	[247]	[247]	[251]	[252]	[257]	[258]	[259]

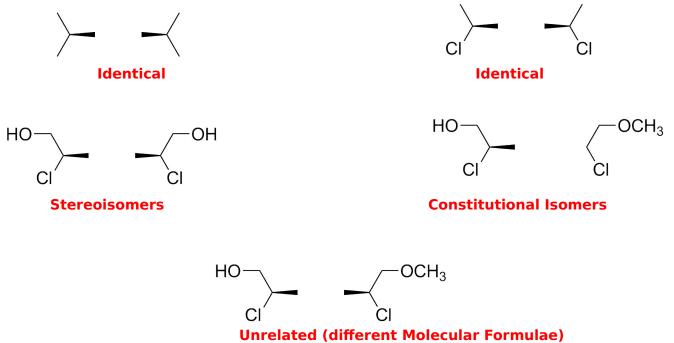




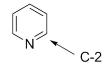
2. (10 points) Identify functional groups present in each of the following molecules. Circle the group and provide a functional group name.



3. (12 points) Identify whether each of the following pairs of molecules are identical, constitutional isomers, stereoisomers, or unrelated.



4. (33 points) Understanding the chemistry of pyridine (C_5H_5N) requires understanding its bonding.



Pyridine (C_5H_5N)

A. If we consider C-2 (one of the carbons bonded to N), describe its geometry, and how will its valence atomic orbitals be hybridized for bonding?

Trigonal geometry (an implied H is present) and therefore sp². One unhybridized p orbital (perpendicular to the molecular plane) will be available for pi bonding.

B. Describe the sigma (σ) component of the C-N bond in terms of which valence atomic orbitals or hybrid orbitals will overlap to form the bonding interaction (use words or any pictures you wish).

Both C and N will be sp² hybridized, so the sigma bond will be the overlap of an sp² hybrid atomic orbital from each atom.

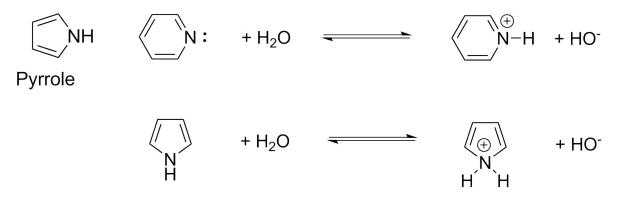
C. Describe the pi (π) component of the C-N bond in terms of which valence atomic orbitals or hybrid orbitals will overlap to form a bonding interaction.

Since each atom will have an unhybridized p prbital perpendicular to the plane of the molecule, these will overlap to form a pi interaction.

D. How would you describe the lone pair on nitrogen in a molecular orbital description? (What kind of MO does it occupy, and where in space is it pointed?)

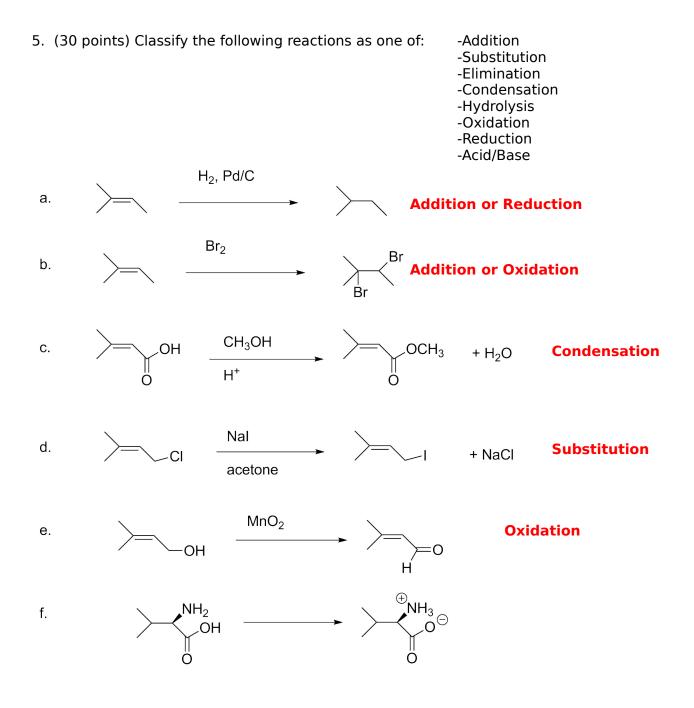
The lone pair will occupy an sp² hybrid lying in the plane of the molecule.

E. Another molecule, pyrrole (C_4H_5N) would at first glance appear to be similar to pyridine but is in fact quite different. Pyridine is a moderately strong base ($pK_b = 8.79$) while pyrrole is an extremely weak base ($pK_b = 17.8$). Suggest a bonding interaction in pyrrole that will change its reactivity and make it less basic.(HINT: Write out the two reactions you need to compare, and draw correct Lewis structures for each compound that account for any lone pairs of electrons.)



When pyridine is protonated, we can draw resonance structures that delocalize the charge. Because the lone pair being protonated is perpendicular to the delocalized pi system, protonation does not change the aromaticity of the molecule.

In pyrrole, however, protonation removes the lone pair that, when shared with the double bond electrons, made the molecule aromatic. There are no additional resonance structures possible to stablize the positive charge. The protonated form is thus highly disfavored, shifting equilibrium to the left.



Selected data that may be of use:

Physical constants:	
$g = 9.8 \text{ m/s}^2$	Gravitational Constant
$\varepsilon_0 = 8.85419 \times 10^{-12} \text{ C}^2/(\text{Nm}^2)$	Electric susceptibility of a vacuum
$c = 2.99792458 \times 10^{10} \text{ cm/s}$	Speed of light
R = 0.08206 L-atm/(mol-K) = 8.314 J/(mol-K)	Gas constant
$N = 6.022 \times 10^{23}$	Avogadro's Number
$k = 1.381 \times 10^{-23} \text{ m}^2\text{kg/(K-s}^2)$	Boltzmann constant
$h = 6.626 \times 10^{-34} m^2 kg/s$	Planck's constant
F = 96485 C/mol	Faraday's constant
$\pi = 3.14159$	
e = 2.71828	

Properties of State

Species	$\Delta H^{\circ}{}_{f}$	S°
N ₂ (g)	0 kJ/mol	191.6 J/(mol-K)
O ₂ (g)	0 kJ/mol	205.1 J/(mol-K)
NO (g)	90.25 kJ/mol	210.8 J/(mol-K)
C (s) (graphite)	0 kJ/mol	5.74 J/(mol-K)
C ₂ H ₂ (g)	226.7 kJ/mol	200.9 J/(mol-K)
C ₆ H ₆ (g)	82.6 kJ/mol	269.3 J/(mol-K)
CO ₂ (g)	-393.5 kJ/mol	213.7 J/(mol-K)
Ag (s)	0 kJ/mol	42.55 J/(mol-K)
Ag+ (aq)	105.6 kJ/mol	72.68 J/(mol-K)
K+(aq)	-254.4 kJ/mol	102.5 J/(mol-K)
Zn (s)	0 kJ/mol	41.63 J/(mol-K)
Zn ⁺² (aq)	-153.9 kJ/mol	112.1 J/(mol-K)
Li (s)	0 kJ/mol	29.12 J/(mol-K)
Li ₂ O (s)	-595.8 kJ/mol	37.89 J/(mol-K)
Cu (s)	0 kJ/mol	33.15 J/(mol-K)
Cu ₂ O (s)	-170 kJ/mol	93 J/(mol-K)

Electromotive series:

TABLE 20.1Some Selected Standard Electrode (Reduction)Potentials at 25 °C

Reduction Half-Reaction

E°,∨

	= , :
Acidic solution	
$F_2(g) + 2e^- \longrightarrow 2F^-(aq)$	+2.866
$O_3(g) + 2 H^+(aq) + 2 e^- \longrightarrow O_2(g) + H_2O(l)$	+2.075
$S_2O_8^{2-}(aq) + 2e^- \longrightarrow 2SO_4^{2-}(aq)$	+2.01
$H_2O_2(aq) + 2 H^+(aq) + 2 e^- \longrightarrow 2 H_2O(1)$	+1.763
$MnO_4^-(aq) + 8 H^+(aq) + 5 e^- \longrightarrow Mn^{2+}(aq) + 4 H_2O(1)$	+1.51
$PbO_2(s) + 4 H^+(aq) + 2 e^- \longrightarrow Pb^{2+}(aq) + 2 H_2O(1)$	+1.455
$Cl_2(g) + 2 e^- \longrightarrow 2 Cl^-(aq)$	+1.358
$Cr_2O_7^{2-}(aq) + 14 H^+(aq) + 6 e^- \longrightarrow 2 Cr^{3+}(aq) + 7 H_2O(1)$	+1.33
$MnO_2(s) + 4 H^+(aq) + 2 e^- \longrightarrow Mn^{2+}(aq) + 2 H_2O(l)$	+1.23
$O_2(g) + 4 H^+(aq) + 4 e^- \longrightarrow 2 H_2O(l)$	+1.229
$2 IO_3^{-}(aq) + 12 H^+(aq) + 10 e^- \longrightarrow I_2(s) + 6 H_2O(l)$	+1.20
$Br_2(1) + 2 e^- \longrightarrow 2 Br^-(aq)$	+1.065
$NO_3^{-}(aq) + 4 H^+(aq) + 3 e^- \longrightarrow NO(g) + 2 H_2O(1)$	+0.956
$Ag^{+}(aq) + e^{-} \longrightarrow Ag(s)$	+0.800
$Fe^{3+}(aq) + e^{-} \longrightarrow Fe^{2+}(aq)$	+0.771
$O_2(g) + 2 H^+(aq) + 2 e^- \longrightarrow H_2O_2(aq)$	+0.695
$I_2(s) + 2e^- \longrightarrow 2I^-(aq)$	+0.535
$Cu^{2+}(aq) + 2e^{-} \longrightarrow Cu(s)$	+0.340
$SO_4^{2-}(aq) + 4 H^+(aq) + 2 e^- \longrightarrow 2 H_2O(1) + SO_2(g)$	+0.17
$\operatorname{Sn}^{4+}(\operatorname{aq}) + 2 \operatorname{e}^{-} \longrightarrow \operatorname{Sn}^{2+}(\operatorname{aq})$	+0.154
$S(s) + 2 H^+(aq) + 2 e^- \longrightarrow H_2S(g)$	+0.14
$2 H^+(aq) + 2 e^- \longrightarrow H_2(g)$	0
$Pb^{2+}(aq) + 2e^{-} \longrightarrow Pb(s)$	-0.125
$\operatorname{Sn}^{2+}(\operatorname{aq}) + 2 \operatorname{e}^{-} \longrightarrow \operatorname{Sn}(\operatorname{s})$	-0.137
$Fe^{2+}(aq) + 2e^{-} \longrightarrow Fe(s)$	-0.440
$Zn^{2+}(aq) + 2e^{-} \longrightarrow Zn(s)$	-0.763
$Al^{3+}(aq) + 3e^{-} \longrightarrow Al(s)$	-1.676
$Mg^{2+}(aq) + 2e^{-} \longrightarrow Mg(s)$	-2.356
$Na^+(aq) + e^- \longrightarrow Na(s)$	-2.713
$Ca^{2+}(aq) + 2e^{-} \longrightarrow Ca(s)$	-2.84
$K^+(aq) + e^- \longrightarrow K(s)$	-2.924
$Li^+(aq) + e^- \longrightarrow Li(s)$	-3.040
Basic solution	
$O_3(g) + H_2O(l) + 2 e^- \longrightarrow O_2(g) + 2 OH^-(aq)$	+1.246
$OCl^{-}(aq) + H_2O(l) + 2 e^{-} \longrightarrow Cl^{-}(aq) + 2 OH^{-}(aq)$	+0.890
$O_2(g) + 2 H_2O(l) + 4 e^- \longrightarrow 4 OH^-(aq)$	+0.401
$2 \operatorname{H}_2 O(1) + 2 \operatorname{e}^- \longrightarrow \operatorname{H}_2(g) + 2 \operatorname{OH}^-(\operatorname{aq})$	-0.828