

EXAMINATION 1
Chemistry 3A

Name: Key
[Print first name before second! Use capital letters!]

Peter Vollhardt
October 5, 2005

Please check the name of your TA and corresponding section number. Complete the remaining information if applicable.

Section #	TA's Name	Section	TA's Name
101	Stefan Minasian	302	Miles Carter
102	Rebecca Lalonde	311	Dan Bachovchin
103	Robin Padilla	312	Laura Miller
111	Melitta Hon	411	Sarah Bell
112	Michael Gribble	412	Dylan Dornaille
113	Tabitha Clem	501	Han Sen Soo
211	Courtney Hastings	502	Nathan Shapiro
212	Philip Morganelli	511	Stavroula Hatzios
301	Cole Witham	512	Katherine Berry

Making up an I Grade _____
(If you are, please indicate the semester during which you took previous Chem 3A: _____).

Please write the answer you wish to be graded in the spaces provided. *Do scratch work on the back of the pages.* This test should have **13** numbered pages. Check to make sure that you have received a complete exam. A good piece of advice: **read carefully over the questions (at least twice); make sure that you understand exactly what is being asked; avoid sloppy structures or phrases. It is better to be pedantic in accuracy now than sorry later! Good Luck!**

DO NOT WRITE IN THIS SPACE

I. _____ (30)

II. _____ (30)

III. _____ (50)

IV. _____ (40)

V. _____ (50)

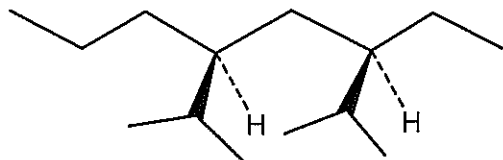
VI. _____ (30)

VII. _____ (20)

Total: _____ (250)

- I. [30 Points] Name or draw, as appropriate, the following molecules according to the IUPAC rules. Indicate stereochemistry where necessary (*cis*, *trans*, *R*, or *S*). Indicate with a circle whether the molecule is chiral or achiral.

a.

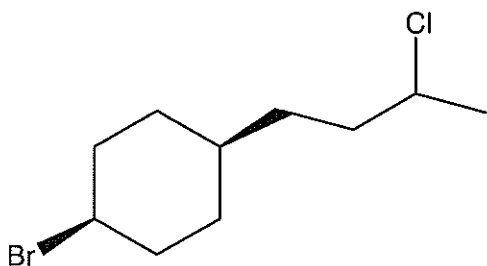


(3R)-Ethyl-2-methyl-
-(5S)-(1-methylethyl)-
octane

chiral

achiral

b.



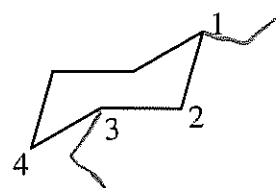
Cis-1-bromo-4-(3-
chlorobutyl)cyclohexane

chiral

achiral

c. *cis*-1,3-Diethylcyclohexane

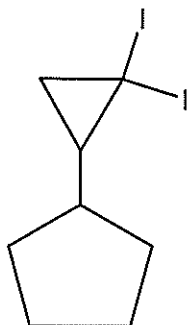
(Draw the more stable conformer)



chiral

achiral

d.

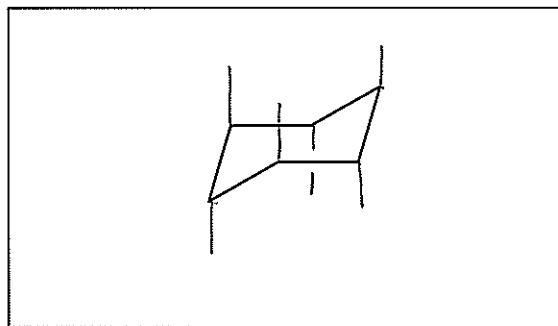


(2,2-Diodocyclopropyl)-
cyclopentane

chiral

achiral

e. All-axial-hexamethylcyclohexane



chiral

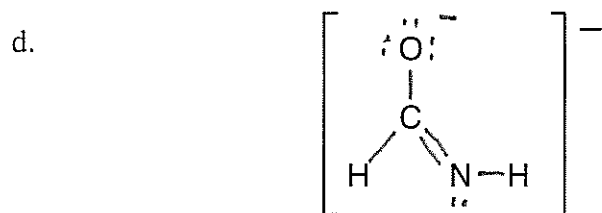
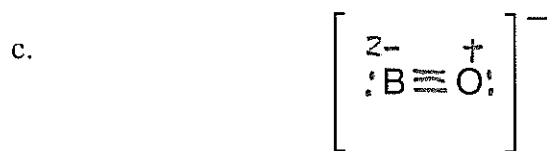
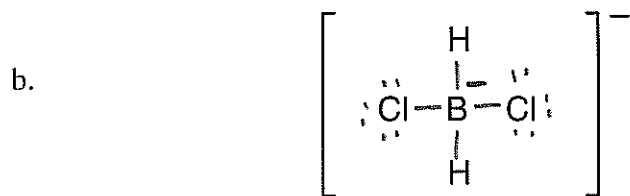
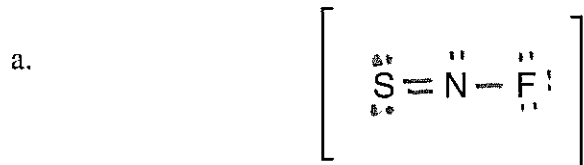
achiral

II. [30 Points] Write the best octet Lewis resonance form for each of the following molecules. Remember to assign charges, if any!

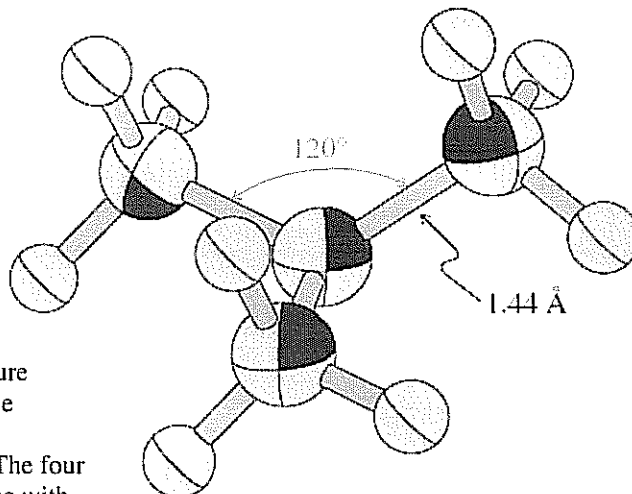
TABLE 1-1 Partial Periodic Table

Period							Halogens	Noble gases
First	H ¹							He ²
Second	Li ^{2,1}	Be ^{2,2}	B ^{2,3}	C ^{2,4}	N ^{2,5}	O ^{2,6}	F ^{2,7}	Ne ^{2,8}
Third	Na ^{2,8,1}	Mg ^{2,8,2}	Al ^{2,8,3}	Si ^{2,8,4}	P ^{2,8,5}	S ^{2,8,6}	Cl ^{2,8,7}	Ar ^{2,8,8}
Fourth	K ^{2,8,8,1}						Br ^{2,8,18,7}	Kr ^{2,8,18,8}
Fifth							I ^{2,8,18,18,7}	Xe ^{2,8,18,18,8}

Note: The superscripts indicate the number of electrons in each principal shell of the atom.

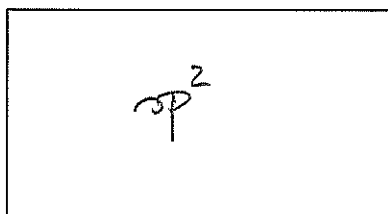


III. [50 Points] The crystal structure of the *tert*-butylation, $(\text{CH}_3)_3\text{C}^+$, is shown below.

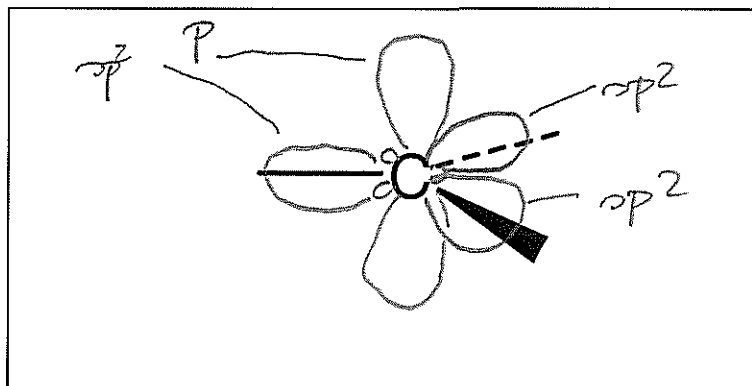


X-ray crystal structure determination for the 1,1-dimethylethyl (*tert*-butyl) cation. The four carbons lie in a plane with 120° C-C-C bond angles.

a. What is the hybridization at the central carbon?



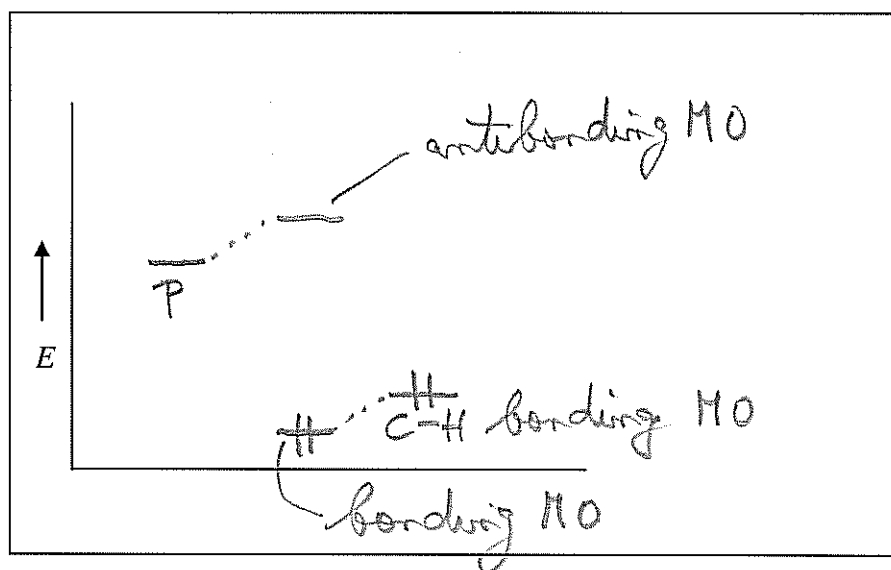
b. Draw the orbitals around the central carbon only (in other words, omit the overlap with the methyl groups) and label them (e.g., s , p , sp^3 , etc.). Indicate in which orbital the charge resides. Use the stencil provided in the box to provide a "grid".



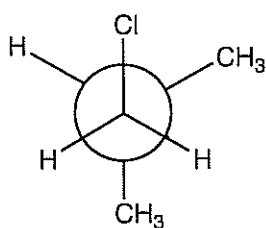
c. Inspection of the structure of the *tert*-butylcation reveals that three of the respective methyl C–H bonds line up perpendicular to the plane containing the four carbons, an arrangement that stabilizes the positive charge. What is the reason for this stabilization? (One word suffices as an answer).

Hyperconjugation

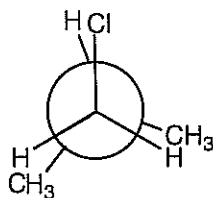
d. Show the orbital splitting associated with this stabilization in an energy level diagram. Label each level clearly [e.g., s , p , sp^3 , bonding molecular orbital (MO), etc.]. Do this for the stabilization by just one of the C–H bonds.



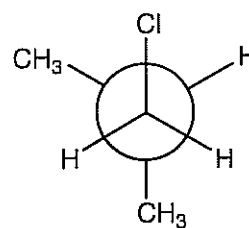
IV. [40 Points] Consider the rotation about the C1–C2 bond in 1-chloro-2-methylpropane, illustrated by the series of Newman projections A–F generated by the sequential clockwise motion of the back-carbon (C2) in increments of 60° .



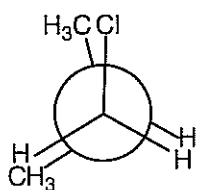
A



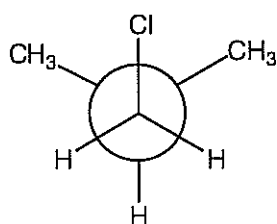
B



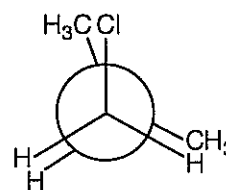
C



D



E



F

a. Indicate, by circling the appropriate letter, the rotamers that contain substituents that are (with respect to each other) anti or gauche, or rotamers that are eclipsed or staggered:

anti:



gauche:



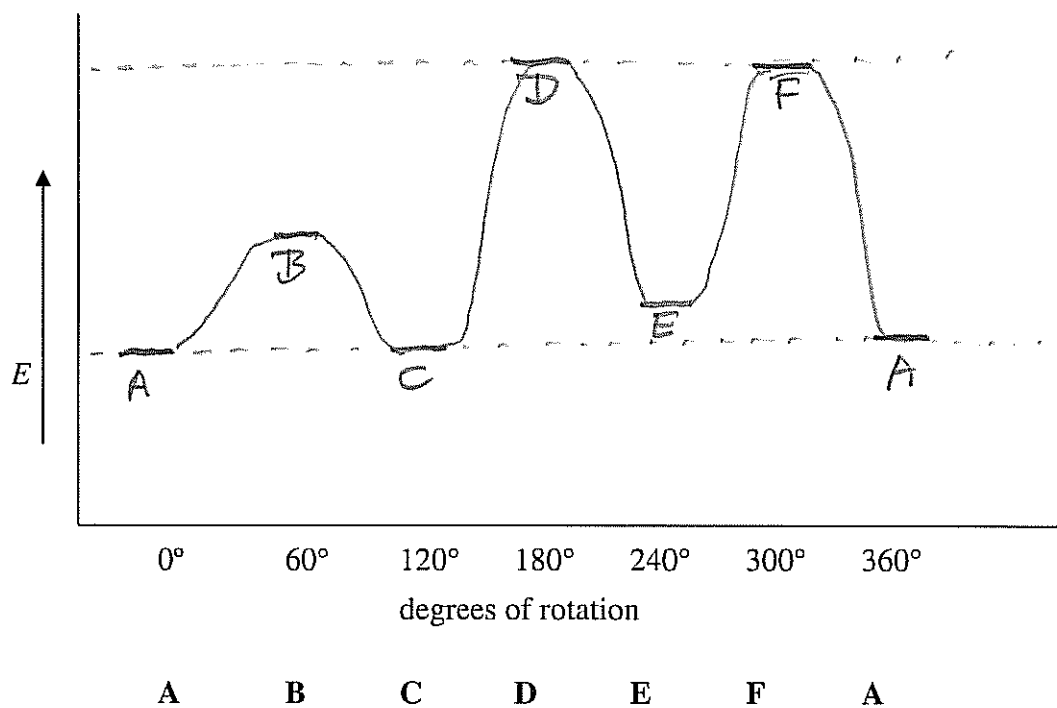
eclipsed:



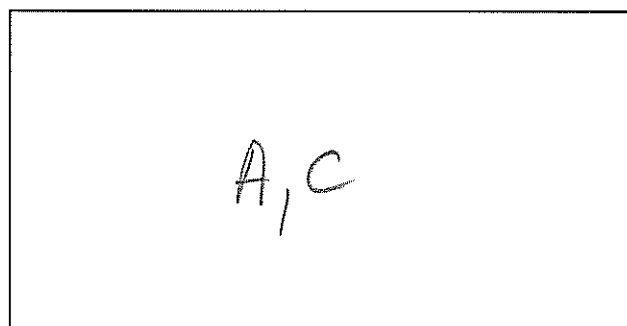
staggered:



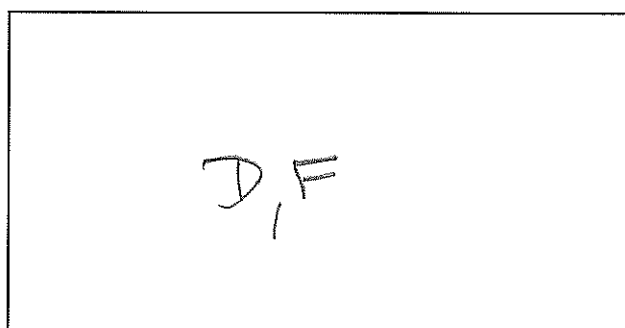
b. Draw a potential energy diagram for this movement. Start by assigning a relative energy to each rotamer on the diagram below, before drawing the interconnecting curve.



c. Two of the staggered rotamers have the same energy. Show which ones by placing the appropriate letters in the box.



d. Two of the eclipsed rotamers have the same energy. Show which ones by placing the appropriate letters in the box.



V. [50 Points] An alternative to chlorine in radical halogenations of alkanes is *tert*-butyl hypochlorite, $(\text{CH}_3)_3\text{COCl}$, as exemplified below for the chlorination of methane (1).

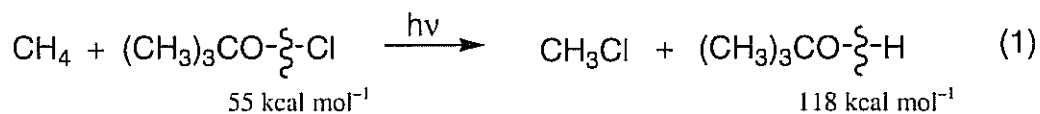


TABLE 3-1

Bond-Dissociation Energies of Various A-B Bonds
(DH° in kcal mol^{-1})

A in A-B	B in A-B						
	-H	-F	-Cl	-Br	-I	-OH	-NH ₂
H—	104	136	103	87	71	119	108
CH ₃ —	105	110	85	70	57	93	84
CH ₃ CH ₂ —	101	111	84	70	56	94	85
CH ₃ CH ₂ CH ₂ —	101	110	85	70	56	92	84
(CH ₃) ₂ CH—	98.5	111	84	71	56	96	86
(CH ₃) ₃ C—	96.5	110	85	71	55	96	85

Note: These numbers are being revised continually because of improved methods for their measurement. Some of the values given here may be in (small) error.

a. Using the bond dissociation energies provided in equation (1) and the Table above, calculate the ΔH° value for reaction (1).

$$\Delta H^\circ (1) : (105 + 55) - (85 + 118) = -43 \text{ kcal mol}^{-1}$$

b. Is the reaction (1) thermodynamically feasible? Circle the right answer.

Answer:

Yes

No

c. Formulate the two propagation steps for reaction (1).

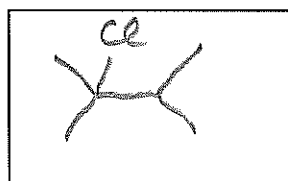
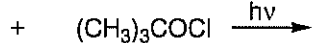
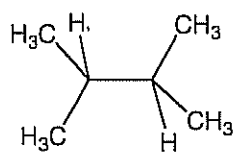
1st Propagation Step :



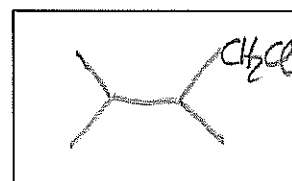
2nd Propagation Step :



d. The selectivity tert : prim in chlorinations with $(\text{CH}_3)_3\text{COCl}$ is 42. Give the products A and B and their ratio in the chlorination of 2,3-dimethylbutane with $(\text{CH}_3)_3\text{COCl}$.

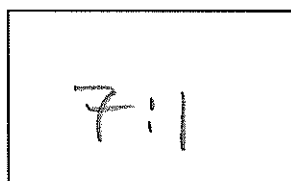


A
(tertiary chlorination)



B
(primary chlorination)

Ratio of A : B =



VI. [30 Points] Compound A undergoes radical bromination to give B and C, among other products.

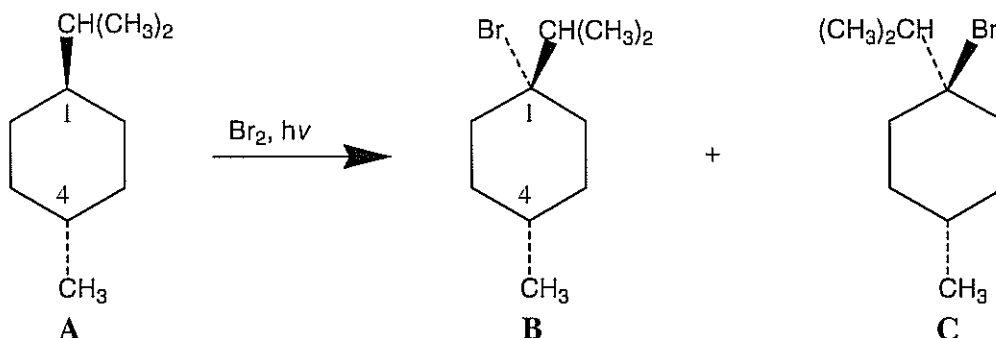
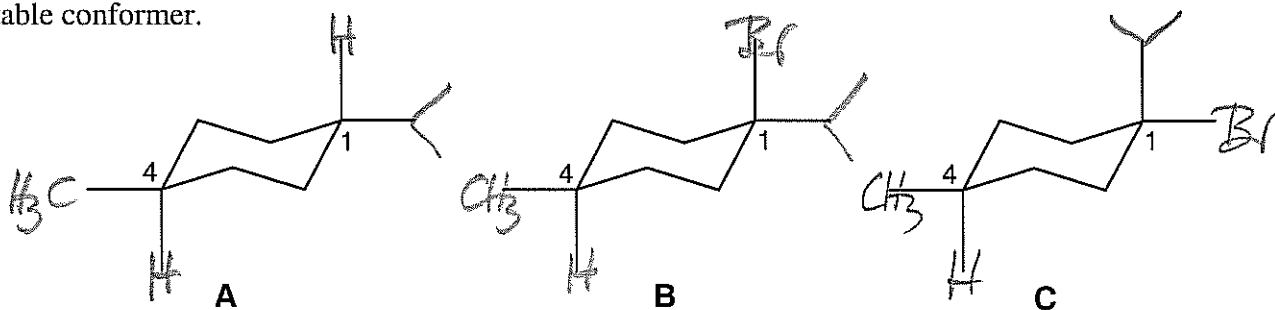


TABLE 4-3 Change in Free Energy on Flipping from the Cyclohexane Conformer with the Indicated Substituent Equatorial to the Conformer with the Substituent Axial			
Substituent	ΔG° (kcal mol ⁻¹)	Substituent	ΔG° (kcal mol ⁻¹)
H	0	F	0.25
CH ₃	1.70	Cl	0.52
CH ₃ CH ₂	1.75	Br	0.55
(CH ₃) ₂ CH	2.20	I	0.46
(CH ₃) ₃ C	≈ 5	HO	0.94
	1.41	CH ₃ O	0.75
	1.29	H ₂ N	1.4

Note: In all examples, the more stable conformer is the one in which the substituent is equatorial.

a. Given the values in the Table and using the cyclohexane stencils provided, show the structures of the most stable conformers of A, B, and C. For each, calculate the free energy of “ring flip” to the less stable conformer.



ΔG° to less
stable conformer

+3.9

+3.35

+0.05

b. Circle the most accurate estimate of the equilibrium constant.

$$K = \frac{A \text{ (more stable conformer)}}{A \text{ (less stable conformer)}} = \text{~1000} \text{ or } \text{~100} \text{ or } \text{~10}$$

VII. [20 Points] Place an X mark in the box designating the most accurate statement.

a. The ΔS° of an organic reaction:



reflects entropy changes



is highly negative for fast transformations

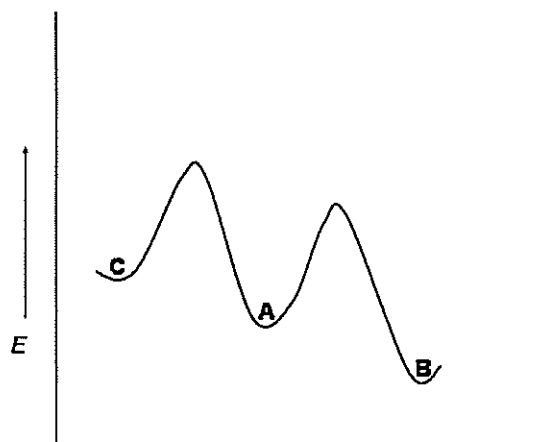


can be estimated by subtracting the sum of the DH° values of the bonds formed from those broken



is the symbol for the rate in the Arrhenius equation

b. When considering the following potential energy diagram:



Compound **A** will convert to **B** faster than it will to **C**.



C is the thermodynamically most stable component of the mixture and will form at the greatest rate from **A** or **B**.



B will convert to **C** faster than **A** will.



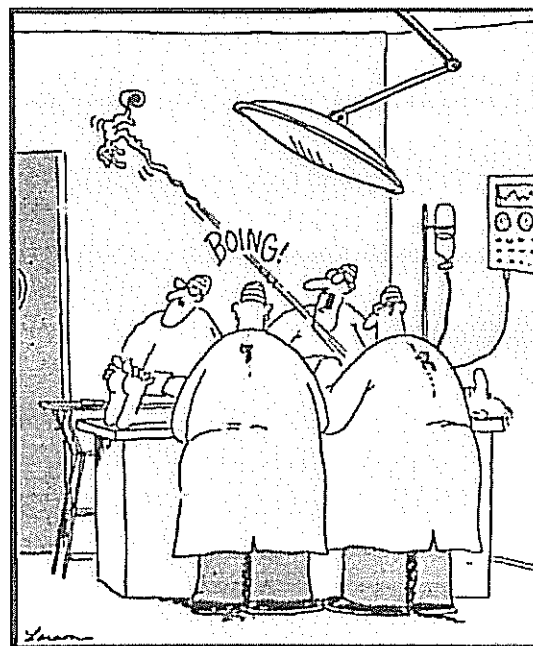
None of the above

c. The compounds *cis*- and *trans*-1,4-dichlorocyclohexane are:

- identical
- stereoisomers
- interconverted by ring flip
- rotamers

d. Acidity H_A increases for element A in the periodic table:

- to the left and up
- to the right and up
- to the right and down
- to the left and down



THEY FLUNKED 3A LAB

* The End *