

University of Windsor
Chemistry and Biochemistry
Chemistry 59-250, Fall Term 2005

Assignment 3

Question #1

Bonding

A researcher in Germany named Driess recently reported a square planar arsonium cation, $[\text{AsR}_4]^+$. Assuming a point group of D_{4h} , use group theory to determine what orbitals may be used for the sigma bonding. From your answer, what kind of hybrid orbitals would be used to make such a molecule according to VBT and how do these compare to the hybrids that you would expect for a normal arsonium cation.

The molecule has D_{4h} symmetry – note: the first C_2 operation in the character table is the one derived from C_4^2 (this is why there is only one in its class), the C_2' lies on the As-R bond axis, the C_2'' lies between the As-R bond axes [when applicable, a single prime after a symmetry operation indicates that the symmetry element contains as many atoms as possible, the double prime means that the symmetry element contains fewer atoms].

D_{4h}	E	$2C_4$	C_2	$2C_2'$	$2C_2''$	i	$2S_4$	σ_h	$2\sigma_v$	$2\sigma_d$
Γ_σ	4	0	0	2	0	0	0	4	2	0

The reducible representation Γ_σ corresponds to the irreducible representation ($A_{1g} + B_{1g} + E_u$) so the orbitals that may be used for σ bonding are: s (A_{1g}), $d_{x^2-y^2}$ (B_{1g}), and the pair $[p_x, p_y]$ (E_u). Since the central atom is As, these would be from the $n = 4$ shell (i.e. 4s, $4d_{x^2-y^2}$, $4p_x$ and $4p_y$). This means that the hybridization of the As atom for this planar arsonium cation would be sp^2d . This is obviously very different from all the other arsonium cations, which have tetrahedral structures and sp^3 hybridization. The primary difference is that, because the atoms must all lie in the same plane, you can not mix in the $4p_z$ orbital (this would make the hybrid orbitals point out of the xy plane) and you have to use an appropriate d orbital that is in the xy plane.

If you had aligned your molecule with the bonds pointing between the x and y axes (on the lines $x = y$ and $x = -y$), you would have had the following reducible representation:

D_{4h}	E	$2C_4$	C_2	$2C_2'$	$2C_2''$	i	$2S_4$	σ_h	$2\sigma_v$	$2\sigma_d$
Γ_σ	4	0	0	0	2	0	0	4	0	2

The reducible representation Γ_σ corresponds to the irreducible representation ($A_{1g} + B_{2g} + E_u$) so the orbitals that may be used for σ bonding are: s (A_{1g}), d_{xy} (B_{2g}), and the pair $[p_x, p_y]$ (E_u). In this case, the appropriate d orbital is $4d_{xy}$, which looks the same as a $4d_{x^2-y^2}$ orbital that has been rotated by 45° .

Question #2

More Bonding

Use group theory to determine what orbitals may be used for (i) the sigma bonding and (ii) the pi bonding in AsF_5 in its most stable geometry. Remember to split the pi bonding into axial, equatorial parallel, and equatorial perpendicular components.

(i)

D_{3h}	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$
Γ_σ	5	2	1	3	0	3

The reducible representation Γ_σ corresponds to the irreducible representation ($2A_1' + E' + A_2''$) so the orbitals that may be used for σ bonding are: s (A_1'), d_{z^2} (A_1'), the pair $[p_x, p_y]$ (E') and p_z (A_2''). Since the central atom is As, these would be from the $n = 4$ shell (i.e. $4s, 4d_{z^2}, 4p_x, 4p_y$ and $4p_z$). This means that the hybridization of the As atom in this molecule would be sp^3d , as you would predict using VBT.

(ii) For π bonding, there are three different sets of vectors to consider. These are vectors for: (a) potential π bonds perpendicular to the equatorial plane (this is considering one type of potential π bonding for the equatorial As-F bonds) $\Gamma_{\pi_{eq\perp}}$; (b) potential π bonds in the equatorial plane (this is considering the other type of potential π bonding for the equatorial As-F bonds) $\Gamma_{\pi_{eq//}}$; and (c) potential π bonds to the axial groups (this is considering both types of potential π bonding for the axial As-F bonds) $\Gamma_{\pi_{ax}}$.

D_{3h}	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$
$\Gamma_{\pi_{eq\perp}}$	3	0	-1	-3	0	1

The reducible representation $\Gamma_{\pi_{eq\perp}}$ corresponds to the irreducible representation ($A_2'' + E''$) so the orbitals that could be used for π bonding perpendicular to the molecular plane are: p_z (A_2'') and the pair $[d_{xz}, d_{yz}]$. Since the p_z orbital has already been used for sigma bonding, the pair of d orbitals would be the best choice for use in pi bonding.

D_{3h}	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$
$\Gamma_{\pi_{eq//}}$	3	0	-1	3	0	-1

The reducible representation $\Gamma_{\pi_{eq//}}$ corresponds to the irreducible representation ($A_2' + E'$) so the orbitals that could be used for π bonding perpendicular to the molecular plane are the pair $[d_{xy}, d_{x^2-y^2}]$ (E') because the A_2' representation does not correspond to any orbitals and we have already used the $[p_x, p_y]$ pair for sigma bonding. Notice that these results are exactly the same as those for the pi bonding in SO_3 in your notes.

D_{3h}	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$
$\Gamma_{\pi_{ax}}$	4	-2	0	0	0	0

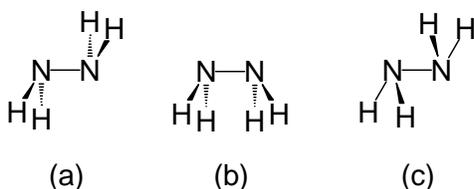
The reducible representation $\Gamma_{\pi_{ax}}$ corresponds to the irreducible representation ($E' + E''$) so the orbitals that could be used for π bonding for the axial bonds are: the pairs $[p_x, p_y]$ (E' – note that the $[d_{xy}, d_{x^2-y^2}]$ pair would not be suitable – make a drawing and you will see why) and $[d_{xz}, d_{yz}]$ (E''). Because we have already used the $[p_x, p_y]$ pair for sigma bonding, the E'' choice would be the most reasonable. Again, make a drawing of the orbitals and you will see why.

Please note: just because we don't draw pi bonds in a Lewis structure does not mean that there isn't pi bonding in a molecule! Symmetry tells us what orbitals we can use to make a pi bond and we have to use our chemical knowledge to determine the nature of the bonding in molecules.

Question #3

Character Tables and Vibrational Spectroscopy

Determine the number of vibrational modes that will be observed in (a) an Infrared experiment and (b) a Raman experiment for hydrazine ($\text{H}_2\text{N-NH}_2$) in each of the following conformations - each one has a different point group:



Since the number of atoms $N = 6$, you have to find $3(6) - 6 = 12$ vibrational modes in each case.

(a) point group: C_{2h}

C_{2h}	E	C_2	i	σ_h
Γ_{tot}	18	0	0	2

The reducible representation for all atomic motion Γ_{tot} yields the irreducible representation ($5A_g + 4B_g + 4A_u + 5B_u$). In C_{2h} , the translational modes have A_u (z) and B_u (x or y) symmetry and the rotational modes have A_g (R_z) and B_g (R_x or R_y) symmetry. Subtracting the 3 translational ($A_u + 2B_u$) and 3 rotational modes ($A_g + 2B_g$) leaves the irreducible representation for the vibrational modes ($4A_g + 2B_g + 3A_u + 3B_u$), which gives 6 IR active modes ($3A_u + 3B_u$) and 6 Raman active modes ($4A_g + 2B_g$), so we would expect to see 6 signals in either of the experiments.

(b) point group: C_{2v}

C_{2v}	E	C_2	σ_v	σ_v'
Γ_{tot}	18	0	2	0

The reducible representation for all atomic motion Γ_{tot} yields the irreducible representation ($5A_1 + 4A_2 + 5B_1 + 4B_2$). In C_{2v} , the translational modes have A_1 (z), B_1 (x) and B_2 (y) symmetry and the rotational modes have A_2 (R_z), B_1 (R_y) and B_2 (R_x) symmetry. Subtracting the 3 translational and 3 rotational modes leaves the irreducible representation for the vibrational modes ($4A_1 + 3A_2 + 3B_1 + 2B_2$), which gives 9 IR active modes ($4A_1 + 3B_1 + 2B_2$) and 8 Raman active modes ($3A_2 + 3B_1 + 2B_2$), so we would expect to see 9 signals in the IR spectrum and 8 signals in the Raman spectrum.

(c) point group: C_2

C_2	E	C_2
Γ_{tot}	18	0

The reducible representation for all atomic motion Γ_{tot} yields the irreducible representation ($9A + 9B$). In C_2 , the translational modes have A (z) and B (x or y) symmetry and the rotational modes have A (R_z) and B (R_x or R_y) symmetry. Subtracting the 3 translational and 3 rotational modes leaves the irreducible representation for the vibrational modes ($7A + 5B$), which gives 12 IR active modes ($7A + 5B$) and 12 Raman active modes ($7A + 5B$), so we would expect to see 12 signals in either of the experiments.

From these results, it is obvious that one can use the number of signals observed experimentally in the vibrational spectra to determine the conformation of $\text{H}_2\text{N-NH}_2$.