Organic Chemistry Students' Use of Stability in Mental Models on Acid and Base Strength

Supporting Information
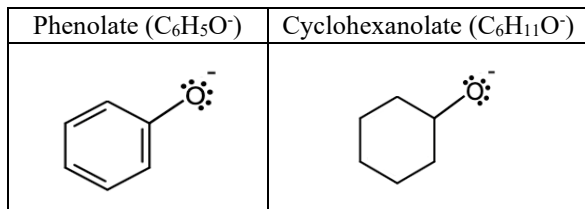
Interview Protocols

Protocol A

Section 1:

Prompt 1: Structures of phenolate ($C_6H_5O^-$) and cyclohexanolate ($C_6H_{11}O^-$) ions are given below.

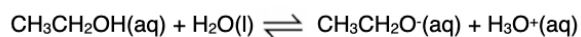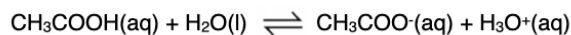| Phenolate ($C_6H_5O^-$)	Cyclohexanolate ($C_6H_{11}O^-$)

Considering the structures, compare the stability of phenolate ($C_6H_5O^-$) and cyclohexanolate ($C_6H_{11}O^-$) ions.

      1.1. **Which ion** (phenolate ($C_6H_5O^-$) and cyclohexanolate ($C_6H_{11}O^-$)) is more stable?

      1.2. Using molecular structures, explain **why** you made such a stability order for phenolate ($C_6H_5O^-$) and cyclohexanolate ($C_6H_{11}O^-$).

Prompt 2: Structures of acetate ion (CH_3COO^-) and structure of ethoxide ion ($CH_3CH_2O^-$) are given below.
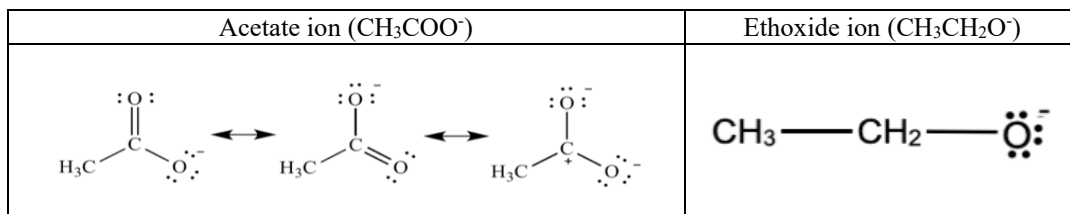
Acetate ion (CH_3COO^-)	Ethoxide ion ($CH_3CH_2O^-$)

Considering the structures, compare the acidity of acetic acid (CH_3COOH) and ethanol (CH_3CH_2OH) in water.

$$CH_3COOH(aq) + H_2O(l) \rightleftharpoons CH_3COO^-(aq) + H_3O^+(aq)$$

$$CH_3CH_2OH(aq) + H_2O(l) \rightleftharpoons CH_3CH_2O^-(aq) + H_3O^+(aq)$$

      2.1 **Which one** (acetic acid (CH_3COOH) and ethanol (CH_3CH_2OH)) is more acidic?

      2.2. Using molecular structures, explain **why** you made such an acidity order for acetic acid (CH_3COOH) and ethanol (CH_3CH_2OH)?

Prompt 3: Structure of acetamide (CH_3CONH_2) and structure of ethylamine ($CH_3CH_2NH_2$) molecules are given below.
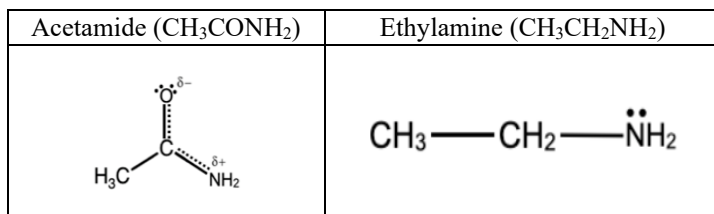
Acetamide (CH_3CONH_2)	Ethylamine ($CH_3CH_2NH_2$)

Considering the structures, compare the basicity of acetamide (CH_3CONH_2) and ethylamine ($CH_3CH_2NH_2$) in water.
    3.1. **Which one** (acetamide (CH_3CONH_2) and ethylamine ($CH_3CH_2NH_2$)) is more basic?
    3.2. Using molecular structures, explain **why** you made such a basicity order for acetamide (CH_3CONH_2) and ethylamine ($CH_3CH_2NH_2$)?

Section 2:

Prompt 1. Structures of Ion A and Ion B are given below. Compare the stability of following ions.

Ion A	Ion B
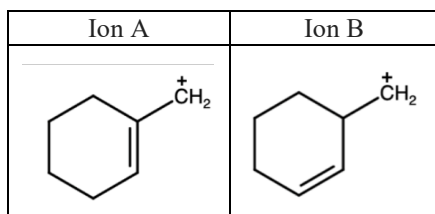
Considering the structures, compare the stability of ion A and ion B.
    1.1 **Which ion** (Ion A and Ion B) is more stable?
    1.2. Using molecular structures, explain **why** you made such a stability order for ion A and ion B.

Prompt 2: Structure of an acid is given below. Compare the acidity of hydrogen atoms.
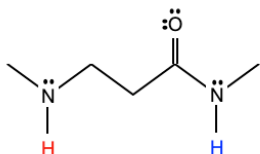
Considering the structure, compare the acidity of hydrogens?
    2.1. **Which hydrogen** (red and blue) is more acidic?
    2.2. Using molecular structure, explain **why** you made such an acidity order for hydrogens (red and blue).

Prompt 3: Structures of propene-1-olate and propoxide are given below. Compare the basicity of following ions.

Propene-1-olate	Propoxide
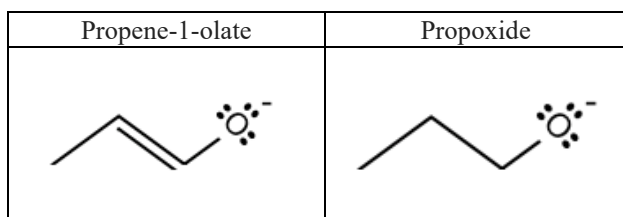
Considering the structures, compare the basicity of propene-1-olate and propoxide in water.
    3.2. **Which one** (propene-1-olate and propoxide) is more basic?
    3.2. Using molecular structures, explain **why** you made such a basicity order for propene-1-olate and propoxide.

Protocol B

Section 1:
Prompt 1: Prompt is the same with the prompt 1 in section 1 in protocol A.

Prompt 2: Structure of acetate ion (CH_3COO^-) and structure of ethoxide ion ($CH_3CH_2O^-$) are given below.

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| Acetate ion (CH$_3$COO$^-$)	Ethoxide ion (CH$_3$CH$_2$O$^-$)

Considering the structures, compare the acidity of acetic acid (CH$_3$COOH) and ethanol (CH$_3$CH$_2$OH) in water.

$$CH_3COOH(aq) + H_2O(l) \rightleftharpoons CH_3COO^-(aq) + H_3O^+(aq)$$

$$CH_3CH_2OH(aq) + H_2O(l) \rightleftharpoons CH_3CH_2O^-(aq) + H_3O^+(aq)$$

2.1. **Which one** (acetic acid (CH$_3$COOH) and ethanol (CH$_3$CH$_2$OH)) is more acidic?
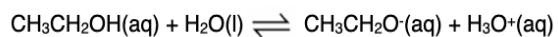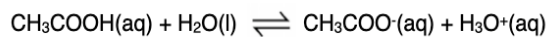2.2. Using molecular structures, explain **why** you made such an acidity order for acetic acid (CH$_3$COOH) and ethanol (CH$_3$CH$_2$OH)?

Prompt 3: Structures of acetamide (CH$_3$CONH$_2$) and structure of ethylamine (CH$_3$CH$_2$NH$_2$) molecules are given below.

Acetamide (CH$_3$CONH$_2$)	Ethylamine (CH$_3$CH$_2$NH$_2$)

Considering the structures, compare the basicity of acetamide (CH$_3$CONH$_2$) and ethylamine (CH$_3$CH$_2$NH$_2$) in water.
3.1. **Which one** (acetamide (CH$_3$CONH$_2$) and ethyl amine (CH$_3$CH$_2$NH$_2$)) is more basic?
3.2. Using molecular structures, explain **why** you made such a basicity order for acetamide (CH$_3$CONH$_2$) and ethylamine (CH$_3$CH$_2$NH$_2$)?

Section 2:

Prompts in this section in protocol B is the same with the prompts in section 2 in protocol A.

Correct Responses for the Case Comparison Tasks in Interviews

<u>**Stability 1**</u>

Phenolate is more stable than cyclohexanolate. When comparing the stability of phenolate vs cyclohexanolate, the relevant factors are;
- Atom is the same therefore size and electronegativity not relevant
- Resonance/delocalization - spreading charge lowers free energy of phenolate
- Inductive effect - Through induction sp^2 carbon groups are electron withdrawing through sigma bonds whereas sp^3 carbon groups are electron donating through sigma bonds. Phenyl group is electron withdrawing which further stabilizes the phenolate ion (by spreading the charge of the anion across a larger area). Cyclo group is electron donating which destabilizes the cyclohexanolate ion (by concentrating negative charge on the oxygen).
- Orbital - The oxygen on phenolate is sp^2 whereas the oxygen on cyclohexanolate is sp^3. The larger s-character on the oxygen on phenolate stabilizes the negative charge on that oxygen relative to the oxygen on the cyclohexanolate.

<u>**Stability 2**</u>

Ion A is more stable than ion B. When comparing the stability of ion A and ion B, the relevant factors are;
- Atom is the same therefore size and electronegativity are not relevant
- Resonance/delocalization - spreading the charge lowers free energy of Ion A
- Inductive effect - Through induction sp^2 carbon groups are electron withdrawing through sigma bonds whereas sp^3 carbon groups are electron donating through sigma bonds. On the left structure the next-door sp^2 carbon is electron withdrawing which destabilizes the carbocation through induction (by concentrating more positive charge at the carbocation). On the right structure the next-door sp^3 carbon is electron donating which stabilizes that carbocation (by spreading the charge of the carbocation across a larger area). Therefore, induction decreases the stability of ion A. That is, this is opposite from the overall stability of these two ions because resonance has a larger effect than induction.
- Orbital is not relevant.

<u>**Acidity 1**</u>

Acetic acid is more acidic than ethanol. When comparing the acidity of acetic acid (CH_3COOH) and ethanol (CH_3CH_2OH) in water, relevant factors are;
- Atom is the same therefore size and electronegativity not relevant.
- Resonance/delocalization - spreading charge lowers free energy and increases stability for conjugate base of acidic acid, which in turn increases the acidity of acetic acid.
- Inductive effect - electron withdrawing of carbonyl group (-C=O) stabilize the acetate ion through polarization of sigma bonds of molecule. Therefore, induction increases stability for conjugate base of acidic acid, which in turn increases the acidity of acetic acid.
- Orbital - The oxygen on acetic acid is sp2 whereas the oxygen on ethanol is sp^3. The larger s-character on the oxygen on acetic acid stabilizes the negative charge on the oxygen of acetate relative to the oxygen of ethoxide. Therefore, induction increases stability for conjugate base of acidic acid, which in turn increases the acidity of acetic acid.

<u>**Acidity 2**</u>

- Blue (amide) hydrogen is more acidic than red (amine) hydrogen. When comparing the acidity of blue (amide) and red (amine) and hydrogen, relevant factors are;
- Atom is the same therefore size and electronegativity are not relevant.
- Resonance/delocalization - spreading charge lowers free energy and increases stability for conjugate base of blue (amide) hydrogen, which in turn increases the acidity of blue hydrogen.

- Inductive effect - electron withdrawing of carbonyl group (-C=O) stabilize the ion formed after donating blue (amide) hydrogen through polarization of sigma bonds of molecule. Therefore, induction increases stability for conjugate base of blue (amide) hydrogen, which in turn increases the acidity of blue (amide) hydrogen.
- Orbital - The nitrogen bonded to blue hydrogen (amide) is sp^2 whereas the nitrogen bonded to red hydrogen (amine) is sp^3. The larger s-character of nitrogen bonded to blue hydrogen (amide) stabilizes the negative charge on the nitrogen of the conjugate base formed after donation of blue hydrogen (amide) relative to the negative charge on nitrogen of the conjugate base formed after donation of the red hydrogen (amine). Therefore, orbital increases stability of conjugate base formed after donation of blue (amide) hydrogen, which in turn increases the acidity of blue (amide) hydrogen.

Basicity 1

Ethylamine is more basic than acetamide. When comparing the basicity of acetamide (CH_3CONH_2) and ethyl amine ($CH_3CH_2NH_2$) in water, relevant factors are;
- Atom is the same therefore size and electronegativity are not relevant.
- Resonance/delocalization - delocalization lowers free energy and hence increases stability of acetamide. Delocalizing the lone pair on nitrogen and giving the nitrogen atom a partial positive charge and makes it less available for bonding a proton for acetamide.
- Inductive effect - electron withdrawing of carbonyl group (-C=O) stabilize the acetamide through polarization of sigma bonds of molecule. Therefore, induction increases stability for acetamide, which in turn decreases the basicity of acetamide.
- Orbital - The nitrogen on acetamide is sp^2 whereas the nitrogen on ethylamine is sp^3. The lone pair on the amide is in a p-orbital, whereas the lone pair on the amine is sp^3. The larger s-character of the lone pair on nitrogen on ethylamine (sp^3) is more stabilizing than on nitrogen on acetamide (p orbital). Therefore, orbital decreases the stability of acetamide, which in turn increases the basicity. That is, this is opposite of the overall effect since delocalization through resonance is a more important factor making the acetamide more stable and thus less basic.

Basicity 2

Propene-1-olate is more basic (less stable) than propoxide. Propanal pKa~17 and propanol pKa~16. When comparing the basicity of propene-1-olate and propoxide in water, relevant factors are;
- Atom - Most important factor in determining basicity. On the propene-1-olate, the negative charge is on both the oxygen and the carbon. The resonance structure drawn contributes more to the overall structure but the other structure does place a decent amount of partial negative charge on the carbon. Negative charge on a less electronegative atom (C) is less stable making the propene-1-olate more basic.
- Resonance/delocalization - making propene-1-olate less basic. Spreading charge lowers free energy and hence increases stability of propene-1-olate. Delocalizing the lone pair on oxygen and giving the oxygen atom less of a negative charge and makes it less available for bonding a proton for propene-1-olate
- Inductive effect - Through induction sp^2 carbon groups are electron withdrawing through sigma bonds whereas sp^3 carbon groups are electron donating through sigma bonds. On propene-1-olate, the next-door sp^2 carbon is electron withdrawing which stabilizes the ion (by spreading the charge of the anion across a larger area). On propoxide, structure the next-door sp^3 carbon is electron donating which destabilizes the anion (by concentrating negative charge on the oxygen). Therefore, propene-1-olate is less basic. Orbital - The oxygen on propene-1-olate is sp^2 whereas the oxygen on propoxide is sp^3. The larger s-character on the oxygen on propene-1-olate stabilizes the negative charge on that oxygen relative to the oxygen on propoxide. Therefore, propene-1-olate is less basic.

Codebook for Granularity

Category	Code	Definition and criteria for inclusion	Examples
Structural	Atom identity	Participants refer to a particular atom(s) by stating the name (e.g., oxygen) and/or symbol (e.g., O, N, C, and H) of the atom(s).	"Because oxygen is electronegative atom. And that makes the whole like, molecule become more electronegative, electronegative…" (S6)
	Atom count	Participants refer to number of particular atom(s) by counting or stating total number.	"…there's two oxygen atoms and one of them has an electronegative charge, there is only one oxygen here" (S1)
	Functional group identity	Participants refer to particular functional group(s) by stating the name (e.g., aromatic ring, amine, amide, carboxyl, carbonyl, hydroxyl, six membered ring with three double bond, carbon ring, benzylic ring, the ring, phenol, phenyl etc.) or formula (e.g., $-NH_2$, $-CONH_2$, $-C=O$) of that functional group(s).	"Um, for me, it was the presence of the carbonyl" (S8)
	Bond type	Participants refer to bond(s) by stating type of bond (e.g., sigma bond/single bond, pi bond/double bond/alkene, single bond has sp^3, double bond has sp^2).	"the only difference is the double bond, so I'd assume the bond would be more strength and then in other one single bond be weaker, which would be more basic." (S4)
	Bond count	Participants refer to number of particular bond(s) by counting (e.g., sigma and pi bond) or stating total number or making inference about hybridization (e.g., sp3, sp2, and sp) based on number of sigma and double bonds.	"acid ion it has. This is 1, 2, 1, 2, 3 bonds" (S6)
	Connectivity of atoms, ions, and functional groups	Participants refer to how atoms, ions, and functional groups are connected either explicitly (e.g., atom, ions, and functional groups are next to or adjacent to or in close proximity or connected to or attached to or bonded to other atoms, ions, and functional groups, a lone pair adjacent to C+,) or implicitly (e.g., Allylic lone pair, Allylic carbocation, lone pair on the atom because the pi bond is just right there, sp^2 is/being closer to CH_2 plus, sp^2 but it's one extra carbon away).	"I know it makes it less stable. I'm not sure as much as to why it makes it less stable. I mostly focused on allylic, but I do know on that greater than flow chart I was talking about vynyllic was like negative below primary." (S11)
	Electron count	Participants refer to number of electron either explicitly by counting or implicitly (e.g., atom with complete/incomplete octet based on number of electrons, lone pairs, valance shell).	"And it has the amine and the amine is here with the complete octet, I think, is a very big indicator to me that it's a more it's more basic compared to that of an Acetamide." (S1)
	Charge	Participants refer to partial or negative charge on the structures explicitly featured.	"Um, for that I looked at I saw in structures two and three, they both had negative charge on the oxygen, but the first one didn't" (S8)
	Resonance specific	Participants refer to explicit features (e.g.,	"the dash, the dash is showing that

	representational feature	double headed arrow, dashed/dotted lines, delta) of structures peculiar to resonance.	the bonds can be formed or broken? And it's basically simultaneous" (S9)
Electronic	Electron withdrawal	Participants refer to electron withdrawal by describing this using various verbs and nouns (e.g., atom withdraws electrons, pull of electrons, pull on the atom, electron withdrawing).	"Yeah. the pull on the on the carbon would be greater than that on the one with the one oxygen and the carbon" (S3)
	Bearing charge	Participants refer to the capacity of bearing charge (e.g., charge is strongly attached to more electronegative atom and atom can hold negative charge better than the other atom).	"Carbon is I mean, they can hold negative charges, but they don't hold them as well as oxygen to. So that's why I would go to Blue hydrogen" (S7)
	Spreading charge	Participants refers to spreading of charge either by explicitly stating how charge is spread (e.g., convert negative charge to a neutral charge, balance out negative charge, neutralize negative charge, charge can be evenly distributed, pull negative charge, resonate charges that can jump around, charge can not really move from the atom over, positive charge would leave that atom then positive charge would be on that atom) and/or the use of a drawing indicating charge separation from formal negative charge on one atom to partial negatives on multiple atoms.	"Oh, and no, I was just saying that the resonance allows it to move the negative charge around and be, and stabilize while the ethoxide, it can't perform resonance" (S2)
	Delocalization of electrons	Participants refer to delocalization of electrons by explicitly stating how electrons are delocalized (e.g., electrons to move around, pi/double bond/s can move, pi bonds can move interchangeably, pi bond can move over here/there and that/this one can move over here/there or that/this one can move up/down, move lone pairs down/up/here/there, change where the electrons are, electrons can shift, delocalization/delocalized electrons, free movement of electrons, do resonance, resonate down, resonance can keep going, how much room the electron could take up and the different positions that it could exist in) and/or the use of a drawing indicating delocalization of electrons.	"Like the double bond could go up to the O and that this could make a pi bond which would then make the nitrogen positive and then that wants to accept" (S12).

Granularity Analysis- Stability

Interviewee	Granularity	Coding for Stability 1	Coding for Stability 2
S1	Structural	Atom identity Connectivity	Connectivity
	Electronic	Delocalization of electrons Spreading charge	
S2	Structural	Functional group identity	Connectivity
	Electronic	Delocalization of electrons Spreading charge	
S3	Structural	Atom identity Connectivity Charge	Atom count Bond count Connectivity
	Electronic	Delocalization of electrons	Spreading of charge Delocalization of electron
S4	Structural	Bond type Charge	Atom count Bond count Connectivity
	Electronic		
S5	Structural	Atom identity Bond type	Bond type Bond count
	Electronic		
S6	Structural	Atom identity Atom count Functional group identity Electron count Charge	Connectivity Electron count Charge
	Electronic	Delocalization of electron	Spreading of charge Delocalization of electron
S7	Structural	Connectivity Functional group identity Charge	Connectivity Electron count Charge
	Electronic	Spreading of charge Delocalization of electron Electron withdrawal	Delocalization of electron
S8	Structural	Atom count Functional group identity Charge	Connectivity
	Electronic	Spreading of charge Delocalization of electron	Spreading of charge Delocalization of electron
S9	Structural	Bond type	Connectivity
	Electronic		
S10	Structural	Connectivity Functional group identity Bond count	Connectivity
	Electronic	Delocalization of electron	Spreading of charge Delocalization of electrons
S11	Structural	Bond count Atom count	Connectivity
	Electronic	Spreading of charge Delocalization of electron	
S12	Structural	Bond type Atom identity Atom count	Bond type Connectivity
	Electronic		Delocalization of electrons
S13	Structural	Connectivity	Atom identity Bond count

			Connectivity
	Electronic	Spreading of charge Delocalization of electron	Spreading of charge Delocalization of electron
S14	Structural	Bond type Electron count Charge	Charge
	Electronic	Spreading of charge Delocalization of electron	Spreading of charge Delocalization of electron

Granularity Analysis- Acidity

Interviewee	Granularity	Coding for Acidity 1	Coding for Acidity 2
S1	Structural	Atom identity Atom count Bond type Charge Resonance specific representational feature	Atom identity Connectivity of atoms, ions, and functional groups
S1	Electronic	Delocalization of electrons Spreading charge	Electron withdrawal
S2	Structural	Atom identity Charge Resonance specific representational feature	Connectivity of atoms, ions, and functional groups
S2	Electronic	Delocalization of electrons Spreading charge	Delocalization of electrons Spreading charge
S3	Structural	Atom identity Atom count Charge Resonance specific representational feature	Atom identity Connectivity of atoms, ions, and functional groups
S3	Electronic	Delocalization of electrons Spreading of charge Electron withdrawal	Delocalization of electrons Electron withdrawal
S4	Structural	Bond type Bond count Charge Electron count Functional group identity	Atom count Bond type Connectivity of atoms, ions, and functional groups
S4	Electronic		
S5	Structural	Resonance specific representational feature	Atom identity Connectivity of atoms, ions, and functional groups
S5	Electronic	Delocalization of electrons	Electron withdrawal
S6	Structural	Atom identity Atom count Bond count Bond type Connectivity of atoms, ions, and functional groups	Atom identity Connectivity of atoms, ions, and functional groups Electron count
S6	Electronic	Electron withdrawal Polarization	Delocalization of electrons
S7	Structural	Functional group identity Resonance specific representational feature	Connectivity of atoms, ions, and functional groups Atom identity Functional group identity
S7	Electronic	Delocalization of electrons	Bearing charge Delocalization of electrons Spreading charge
S8	Structural	Atom identity Charge Resonance specific representational feature	Functional group identity
S8	Electronic	Delocalization of electrons Spreading charge	Delocalization of electrons Spreading charge
S9	Structural	Atom identity Atom count Charge	Atom identity Connectivity of atoms, ions, and functional groups
S9	Electronic		
S10	Structural	Atom identity	Connectivity of atoms, ions, and functional

		Charge Resonance specific representational feature	groups
	Electronic	Delocalization of electrons	Delocalization of electrons
S11	Structural	Charge Resonance specific representational feature	Connectivity of atoms, ions, and functional groups
	Electronic	Delocalization of electrons	Delocalization of electrons
S12	Structural	Atom identity Atom count Charge	Connectivity of atoms, ions, and functional groups
	Electronic		Delocalization of electrons Electron withdrawal
S13	Structural	Charge Resonance specific representational feature	Connectivity of atoms, ions, and functional groups
	Electronic	Delocalization of electrons Spreading charge	Delocalization of electrons
S14	Structural	Charge Resonance specific representational feature	Connectivity of atoms, ions, and functional groups
	Electronic	Delocalization of electrons Spreading charge	Delocalization of electrons

Granularity Analysis- Basicity

Interviewee	Granularity	Coding for Basicity 1	Coding for Basicity 2
S1	Structural	Charge Electron count Functional group identity	Bond type
	Electronic		Delocalization of electrons
S2	Structural	Atom identity Charge Electron count	Connectivity of atoms, ions, and functional groups
	Electronic		Delocalization of electrons Spreading charge
S3	Structural	Atom identity Charge Electron count Resonance specific representational feature	Connectivity of atoms, ions, and functional groups
	Electronic	Delocalization of electrons Polarization	Delocalization of electrons
S4	Structural	Atom identity Bond type Bond count Charge Functional group identity	Atom identity Atom count Bond type Charge
	Electronic		
S5	Structural	Charge Electron count Functional group identity	Bond type
	Electronic		
S6	Structural	Atom identity Atom count Electron count Functional group identity	Atom count Electron count
	Electronic		Delocalization of electrons Spreading charge
S7	Structural	Atom identity Charge Resonance specific representational feature	Bond type Charge Connectivity of atoms, ions, and functional groups
	Electronic		Delocalization of electrons Spreading charge
S8	Structural	Atom identity Charge Electron count Resonance specific representational feature	Bond type
	Electronic	Delocalization of electrons Spreading charge	Delocalization of electrons
S9	Structural	Atom identity Bond type Charge Electron count Resonance specific representational feature	Connectivity of atoms, ions, and functional groups
	Electronic	Delocalization of electrons	
S10	Structural	Charge Resonance specific representational feature	Bond type
	Electronic	Delocalization of electrons	

		Spreading charge Electron withdrawal	
S11	Structural	Atom identity Charge Electron count	Bond count Charge Electron count
	Electronic	Delocalization of electrons Spreading charge	Delocalization of electrons
S12	Structural	Bond type Resonance specific representational feature	Connectivity of atoms, ions, and functional groups
	Electronic	Delocalization of electrons Spreading charge	Delocalization of electrons
S13	Structural	Atom identity	Bond type
	Electronic	Bearing charge Delocalization of electrons	Delocalization of electrons
S14	Structural	Charge Functional group identity Electron count	Bond type
	Electronic		