

Resonance

RESONANCE

It is delocalisation of electrons in a conjugated system.

Important Terminology used in Resonance :

- (a) Curved arrows
- (b) Conjugation system
- (c) Localized & delocalized electron

CURVED ARROWS : THE TOOLS FOR DRAWING RESONANCE STRUCTURES

Every curved arrow has a head and a tail. It is essential that the head and tail of every arrow be drawn in precisely the proper place. The tail shows where the electrons are coming from, and the head shows where the electrons are going (remember that the electrons aren't really going anywhere, but we treat them as if they were so we can make sure to draw all resonance structures) :



Or it must point to an atom to form a lone pair.



Never draw the head of an arrow going off into space :



Let's focus on one at a time :

C-1. Never break a single bond when drawing resonance structures. By definition, resonance structures must have all the same atoms connected in the same order. Otherwise, they would be different compounds.



C-2. Never violate the octet rule. Let's review the octet rule. Atoms in the second period (C, N, O, F) have only four orbitals in their valence shell.



In each of these drawings, the central atom cannot form another bond because it does not have a fifth orbital that can be used. This is impossible. Don't ever do this.

Solved Examples

 For each of the problems below, determine which arrows violate either one of the two commandments C-1 or C-2, and explain why. (Don't forget to count all hydrogen atoms and all lone pairs. You must do this to solve these problems.)



DRAWING GOOD ARROWS

Now, we need to know where to put the head of the arrow. We look for any lone pairs or double bonds that are appearing. We see that there is a new lone pair appearing on the oxygen. So now we know where to put the head of the arrow :



For below example, we need two arrows. Let's start at the top. Loose a lone pair from the oxygen and form a C O. Let's draw that arrow :

Notice that if we stopped here, we would be violating the second commandment C-2. The central carbon atom is getting five bonds. To avoid this problem, we must immediately draw the second arrow. The C C disappears (which solves our octet problem) and becomes a lone pair on the carbon. Now we can draw both arrows :



Solved Examples

For each drawing, try to draw' the curved arrow's that get you from one drawing to the next. In many cases you will need to draw more than one arrow.



Solved Example

Draw the resonance structure that you get when you push the arrows shown below. Be sure to include formal charges.





Ans. We read the arrows to see what is happening. One of the lone pairs on the oxygen is coming down to form a bond, and the C C double bond is being pushed to form a lone pair on a carbon atom. This is very similar to the example we just saw.

We just get rid of one lone pair on the oxygen, place a double bond between the carbon and oxygen, get rid of the carbon-carbon double bond, and place a lone pair on the carbon. Finally, we must put in any formal charges :



CONJUGATED SYSTEMS

In the dictionary, 'conjugated' is defined, as joined together, especially in pairs' and 'acting or operating as if joined'. This does indeed fit very well with the behaviour of such conjugated double bonds since the properties of a conjugated system are often different from those of the components parts. We are using *conjugation* to describe bonds and *delocalization* to describe electrons.

We shall use conjugation and delocalization : conjugation focuses on the sequence of alternating double and single bonds while delocalization focuses on the molecular orbitals covering the whole system. Electrons are delocalized over the whole of a conjugated system.









- Ans. All have conjugated system.
 - Are these molecules conjugated? Explain your answer in any reasonable way.



Ans. Only 1 of the above is conjugated.

LOCALIZED & DELOCALIZED ELECTRON

Electrons that are restricted to a particular region are called localized electrons. Localized electrons either belong to a single atom or are confined to a bond between two atoms.



Many organic compounds contain delocalized electrons. Delocalized electrons neither belong to a single atom nor are confined to a bond between two atoms-they are electrons that are shared by more than two atoms.

The rest of this chapter concerns molecules with more than one C — C double bond and what happens to the orbitals when they interact. To start, we shall take a bit of a jump and look at the structure of benzene. Benzene has been the subject of considerable controversy since its discovery in 1825. It was soon worked out that the formula was C_6H_6 , but how were these atoms arranged? Some strange structures were suggested until Kekulé proposed the correct structure in 1865.





Kekule's structure for benzene

With benzene itself, these two forms are equivalent but,



2-bromobenzoic acid

'6'-bromobenzoic acid

R

CO₂H

If the double bonds were localized then these two compound would be chemically different. (the double bonds are drawn shorter than the single bonds to emphasize the difference)

If we had a 1,2- or a 1,3-disubstituted benzene compound, these two forms would be different. A synthesis was designed for these two compounds but it was found that both compounds were identical. This posed a bit of a problem to Kekulé—his structure didn't seem to work after all. His solution was that benzene rapidly equilibrates, or 'resonates' between the two forms to give an averaged structure in between the two.



resonance contributor

resonance contributor



resonance hybrid

Only if all the atoms sharing the delocalized electrons lie in or close to the same plane so their *p* orbitals can effectively overlap. For example, cyclooctatetraene is not planar-it is tub-shaped.



Alternatively, an average of Lewis structures is sometimes drawn using a dashed line to represent a "partial" bond. In the dashed-line notation the central oxygen is linked to the other two by bonds that are halfway between a single bond and a double bond, and the terminal oxygens each bear one half of a unit negative charge.



Rules for Writing Resonance Structures :

1. Resonance structures exist only on paper : Although they have no real existence of their own, resonance structures are useful because they allow us to describe molecules, radicals, and ions for which a single Lewis structure is inadequate. We write two or more Lewis structures, calling them resonance structures or resonance contributors. We connect these structures by double-headed arrows (), and we say that the hybrid of all of them represents the real molecule, radical, or ion.

2. In writing resonance structures, we are only allowed to move electrons : The positions of the nuclei of the atoms must remain the same in all of the structures. For example, Structure 3 is not a resonance structure for the allylic cation, because in order to form it we would have to move a hydrogen atom and this is not permitted :

$$CH_3 \xrightarrow{\oplus} CH \xrightarrow{\oplus} CH_2 \xrightarrow{\oplus} CH_3 \xrightarrow{\oplus} CH \xrightarrow{=} CH \xrightarrow{+} CH_2$$

These are resonance structures for the allylic cation formed when 1, 3-butadiene accepts a proton.

^сH₂—СH₂—СH=СH₂

This is not a proper resonance structure for the allylic cation because a hydrogen atom has been moved.

Generally speaking, when we move electrons we move only those of bond (as in the example above) and those of lone pairs.

(a) Move electrons toward a positive charge or toward a bond.

$$CH_2 \stackrel{+}{=} CH \stackrel{+}{\to} CHCH_3 \longleftrightarrow CH_2 - CH = CHCH_3$$

localized electrons

3. All of the structures must be proper Lewis structures : We should not write structures in which carbon has five bonds, for example :



We cannot draw this resonance structure :



The nitrogen atom would have five bonds, which would violate the octet rule.

(b) Move a nonbonding pair of electrons toward a bond.

 $CH_3CH \rightarrow CH_3CH - CH = \dot{N}HCH_3$

delocalized electrons

an sp^3 hybridized carbon cannot accept electrons СН₃СН=СН-

localized electrons

an *sp*³ hybridized carbon cannot accept electrons

CH2CHCH3 CH₂

delocalized electrons



4. All resonance structures must have the same number of unpaired electrons : The following structure is not a resonance structure for the allyl radical because it contains three unpaired electrons and the allyl radical contains only one :



5. All atoms that are a part of the delocalized -electron system must lie in a plane or be nearly planar : For example, 2,3-di-tert-butyl-1,3-butadiene behaves like a non-conjugated diene because the large tert-butyl groups twist the structure and prevent the double bonds from lying in the same plane. Because they are not in the same plane, the p orbitals at C₂ and C₃ do not overlap and delocalization (and therefore resonance) is prevented :



2, 3-Di-tert-butyl-1,3-butadiene

The bond contains two electrons and, since we fill up the energy level diagram from the lowestenergy orbital upwards, both these electrons go into the bonding molecular orbital. In order to have a strong bond, the two atomic *p* orbitals must be able to overlap effectively. This means they must be parallel.



the two p orbitals can only overlap if they are parallel

6. The energy of the actual molecule is lower than the energy that might be estimated for any contributing structure : The actual allyl cation, for example, is more stable than either resonance structure 4 or 5 taken separately would indicate. Structures 4 and 5 resemble primary carbocations and yet the allyl cation is more stable (has lower energy) than a secondary carbocation.

$$CH_2 = CH - \overset{+}{C}H_2 \longleftrightarrow \overset{+}{C}H_2 - CH = CH_2$$

We shall find that benzene is highly resonance stabilized because it is a hybrid of the two equivalent forms that follow :



Resonance structures for benzene

Representation of hybrid

- 7. Equivalent resonance structures make equal contributions to the hybrid, and a system describe by them has a large resonance stabilization : Structures 4 and 5 make equal contributions to the allylic cation because they are equivalent. They also make a large stabilizing contribution and account for allylic cations being unusually stable. The same can be said about the contributions made by the equivalent structures for benzene.
- 8. The more stable a structure is (when taken by itself), the greater is its contribution to the hybrid : Structures that are not equivalent do not make equal contributions. For example, the following cation is a hybrid of structures 6 and 7. Structure 6 makes a greater contribution than 7 because structure 6 is a more stable tertiary carbocation while structure 7 is a primary cation :

$$\overset{CH_3}{\overset{l_b}{\overset{c}{\leftarrow}}}_{H_3} \overset{CH_3}{\overset{l_b}{\overset{c}{\leftarrow}}}_{\overset{CH_3}{\overset{c}{\leftarrow}}} \overset{CH_3}{\overset{l_1}{\overset{l_2}{\leftarrow}}}_{H_2} = \begin{bmatrix} \overset{CH_3}{\overset{l_3}{\overset{c}{\leftarrow}}}_{H_3} \overset{CH_3}{\overset{l_3}{\overset{c}{\leftarrow}}}_{H_3} \overset{CH_3}{\overset{l_3}{\leftarrow}}_{H_3} \overset{CH_3}{\overset{L_3}{\leftarrow}}_$$

That **6** makes a larger contribution means that the partial positive charge on carbon **b** of the hybrid will be larger than the partial positive charge on carbon **d**. It also means that the bond between carbon atoms **c** and **d** will be more like a double bond than the bond between carbon atoms **b** and **c**.

 Resonance forms do not differ in the position of nuclei. The two structures given below are not resonance forms because the position of the carbon and hydrogen atoms outside the ring are different in the two forms.



Another Example is of the structural formulas

11.



which represent different compounds, not different resonance forms of the same compound. A is a Lewis structure for nitromethane; B is methyl nitrite.

10. Only the placement of the electrons may be shifted from one structure to another. (Electrons in double bonds and lone pairs are the ones that are most commonly shifted.) Nuclei cannot be moved, and the bond angles must remain the same.



Yes : Does not violate the octet rule.

DRAWING RESONANCE STRUCTURES— BY RECOGNIZING PATTERNS

There are five patterns that you should learn to recognize to become proficient at drawing resonance structures. First we list them, and then we will go through each pattern in detail, with examples and exercises. Here they are :

- 1. A lone pair next to a pi bond.
- **2.** A lone pair next to a positive charge.
- 3. A pi bond next to a positive charge.
- 4. A pi bond between two atoms, where one of those atoms is electronegative.
- 5. Pi bonds going all the way around a ring.

A LONE PAIR NEXT TO A PI BOND

Let's see an example before going into the details :



The atom with the lone pair can have no formal charge (as above), or it can have a negative formal charge as below :



The important part is having a lone pair "next to" the pi bond. "Next to" means that the lone pair is separated from the double bond by exactly one single bond—no more and no less. You can see this in all of the examples below:



In each of these cases, you can bring down the lone pair to form a pi bond, and kick up the pi bond to form a lone pair



Notice what happens with the formal charges. When the atom with the lone pair has a negative charge, then it transfers its negative charge to the atom that will get a lone pair in the end :



When the atom with the lone pair does not have a negative charge to begin with, then it will end up with a positive charge in the end, while a negative charge will go on the atom getting the lone pair in the end (remember conservation of charge):



Solved Examples



resonance contributors of pyrrole

Cyclopentadienyl anion





Sol. The following represent the resonance forms of the acetylacetone anion:



Sol. The following represent the resonance forms of the nitroacetone anion :



Please note that while nitro groups are so electron withdrawing that delocalization of their associated positive charge plays a minimal role in any family of resonance structures, this delocalization is technically possible. Try to identify additional resonance structures where the positive charge is delocalized.

Use a three-dimensional drawing to show where the electrons are pictured to be in each resonance form.
(a) HCONH₂



Notice that the lone pair needs to be directly next to the pi bond. If we move the lone pair one atom away, this does not work anymore :



A LONE PAIR NEXT TO A POSITIVE CHARGE

Let's see an example :

The atom with the lone pair can have no formal charge (as above) or it can have negative formal charge :



The important part is having a lone pair next to a positive charge. In each of the below cases, we can bring down the lone pair to form a pi bond:



Notice what happens with the formal charges. When the atom with the lone pair has a negative charge, then the charges end up canceling each other:



When the atom with the lone pair does not have a negative charge to begin with, then it will end up with the positive charge in the end (remember conservation of charge):



Solved Examples



A PI BOND NEXT TO A POSITIVE CHARGE



Notice what happens to the formal charge in the process. It gets moved to the other end:



It is possible to have many double bonds in conjugation (this means that we have many double bonds that are each separated by only one single bond) next to a positive charge:



When this happens, we can push all of the double bonds over, and we don't need to worry about calculating formal charges-just move the positive charge to the other end:



Of course, we should push one arrow at a time so that we can draw all of the resonance structures. But it is nice to know how the formal charges will end up so that we don't have to calculate them every time we push an arrow.

Solved Examples



Solved Examples



DRAWING THE DICATION

The dication still has the same number of atoms as the neutral species with only fewer electrons. Where have the electrons been taken from? The system now has two electrons less. We could draw a structure showing two localized positive charges but this would not be ideal since the charge is spread over the whole ring system.







one structure with localized charges

the charges can be delocalized all round the ring

structure to show equivalence of all the carbon atoms

Representations of the allyl cation



curly arrows show the positive charge is shared over both the end atoms

Do not confuse this delocalization arrow with the equilibrium sign. A diagram like this would be wrong :



A PI BOND BETWEEN TWO ATOMS, WHERE ONE OF THOSE ATOMS IS ELECTRONEGATIVE (N, O, ETC.)



As another example, consider the structure below. We cannot move the C C bond to become another bond unless we also move the C O bond to become a lone pair :



In this way, we truly are "pushing" the electrons around.

PI BONDS BETWEEN SIMILAR ATOMS

Whenever we have alternating double and single bonds, we refer to the alternating bond system as conjugated:

PI BONDS GOING ALL THE WAY AROUND A RING

When we have a conjugated system that wraps around in a circle, then we can always move the electrons around in a circle:



It does not matter whether we push our arrow's clockwise or counterclockwise (either way gives us the same result, and remember that the electrons are not really moving anyway).

Solved Examples

▶ For each of the compounds below, locate the pattern we just learned and draw the resonance structure.





























ESTIMATING THE RELATIVE STABILITY OF RESONANCE STRUTURES

(a) The more covalent bonds a structure has, the more stable it is. We know that forming a covalent bond lowers the energy of atoms. 8 is by far the most stable and makes by far the largest contribution because it contains one more bond.



(b) Structures in which all of the atoms have a complete valence shell of electrons are especially stable and make large contributions to the hybrid.



(c) Charge separation decreases stability Separating opposite charges requires energy. Therefore, structures in which opposite charges are separated have greater energy (lower stability) than the those that have no charge separation. This means that of the following two structures for vinyl chloride, structure 13 makes a larger contribution because it does not have separated charge. (This does not mean that structure 14 does not contribute to the hybrid, it just means that the contribution made by 14 is smaller.

$$CH_2 = CH - \overset{\bullet}{CH} : \longleftrightarrow : \overline{C}H_2 - CH = \overset{\bullet}{CH} : \overset{\bullet}{H}_2 - CH = \overset{\bullet}{CH} : \overset{\bullet}{H} : \overset{\bullet$$

- (d) Resonance contributors with negative charge on highly electronegative atoms are more stable than ones with negative charge on less or nonelectronegative atoms. Conversely, resonance contributors with positive charge on highly electronegative atoms are less stable than ones with positive charge on nonelectronegative atoms.
- (e) To predict the energies of the resonance structures, we consider the energy of resonance hybrid structure. Resonance hybrid is the weighted average of the resonance contributors. The following structures are considered relatively stable:
 - (i) Structures having filled octets for second row elements (C, N, O, F) are stable.
 - (ii) Structures having minimum number of formal charges and maximum number of bonds.
 - (iii) Structure in which negative charge is on the most electronegative atom (C<N<O).
 - (iv) Structure in which there is minimal charge separation while keeping the formal charges closer together.

Solved Examples

Which of the following structures is relatively stable?



Ans. Structure (A) is most stable as it follows all guidelines as per points (a) to (e).

Structure (B) is more stable as it violates point (a).

Structure (C) is least stable for violating point (a) and primary carbocation. Stability order is A > B > C

Solved Examples

The carbon monoxide molecule is unusual and interesting in many ways. A collection of examples of relative stability of resonance forms is found in the diagram below. You should go through them very carefully and see if you can understand them and make the same predictions that you see here.



Solved Examples

• The following Lewis/Kekule structures (A) – (L) are isomeric (with molecular formula CN_2H_2).

Which of these structures match the following properties ? Indicate with letters (A) to (L). If no structure fit the property write the letter X.

- 1. Which of the structures have no atoms with formal charge?
- 2. Which of the structures have at least one nitrogen atom with a(+) formal charge
- 3. Which of the structure have at least one nitrogen atom with a(-) formal charge?
- 4. Which of the structures have at least one carbon atom with a(+) formal charge?
- 5. Which of the structures have at least one carbon atom with a(-) formal charge?
- 6. Which of the structures have electron deficient heavy atoms (N or C)?
- Ans. 1. (B, C, G), 2. (A, D, E, F, H, J), 3. (A, D, K, L), 4. (K, L), 5 (F, E, H, J), 6. (B, I, K, L).
 - Write the possible resonance structures for the following molecules. Show the direction of the movement of electrons with the help of arrows.









SCHEMATIC ENERGY LEVEL DIAGRAMS OF SOME MESOMERIC MOLECULES/IONS

Energy diagrams of some resonating structures are given as follows. (Note: The downwards arrow marks the conventional mesomeric energies and indicates energy level).

Solved Examples

Carboxylate ion



Interpretation : The two equivalent resonating structures have the same energy.

Carbonate ion



Carbonate ion

Interpretation : The three equivalent resonating structures have the same energy.

Carbon dioxide



Interpretation : Polarized structures have higher energy because separation of opposite charges requires energy.

Alkylcyanate



Alkyl cyanate

Interpretation : Negative charge on the more electronegative element (oxygen) makes the structure more stable.

Vinyl ether



Interpretation : Separation of opposite charges requires energy.

▶ But-1,3-diene



Interpretation : Unlike charges must be closer to each other for the structure to be more stable. Ethanoic acid



Ethanoic acid



- (A) 7 (B) 8 (C) 9 (D) 10
- 4. The compound shown to the right is known as Dewar Benzene. What relationship does this compound bear to benzene?



- (A) It is a resonance structure of benzene
- (B) It is an enantiomer of benzene
- (C) It bears no relationship to benzene
- (D) It is a structural isomer of benzene
- 5. Choose the answer that has the molecular orbitals for the allyl anion (CH₂ CH CH₂) correctly identified.



6. When benzene is protonated the resulting ion is the cyclohexadienyl cation. Which of the following MOs is the best representation of the LUMO of this cation?



7. Choose the order that has the followingC = O groups correctly arranged with respect to increasing resonance stabilization.



8. Which of the following pairs are resonance contributors?



- (D) All of the above
- 9. Which of the following are not resonating structures of each other?



- (D) CH₃CH CH CH CH CH₂ and CH₃CH CH CH CH CH₂
- 10. Which of the following is not resonating structure of each other?





11. Which of the following compound is not resonance stabilized?





(D) 5

17. Which of the carbocation is not resonance stabilized?





30. Number of Resonating structures having 2° carbocation



35. Which of the following pairs of structures do not represent resonance forms?



36. Which of the following resonance structure contributes the most to the resonance hybrid?



UNSOLVED EXAMPLES

1. Which of the following pairs of structures represent resonance forms, and which do not? Explain.



CH₃

2. 1,3-Cyclobutadiene is a rectangular molecule with two shorter double bonds and two longer single bonds. Why do the following structures not represent resonance forms?

CH₂CH₃



3. Which of the following pairs represent resonance Structures?



- 4. Naphthalene, has three resonance forms. Draw them.
- 5. Are the following pairs of structures resonance contributors or different compounds?



- **6.** Write the contributing resonance structures and the delocalized hybrid for (a) BCl₃, (b) H₂CN₂ (diazomethane).
- 7. Circle the conjugated atoms of ciprofloxacin.

One circle per atom



8. How many conjugated atoms (marked with)



9. Consider structural formulas A, B, C and D :

$$H - \overset{\circ}{C} = N = \overset{\circ}{O}: \qquad H - C \equiv N - \overset{\circ}{O}: \qquad H - C \equiv N = \overset{\circ}{O}: \qquad H - C = \overset{\circ}{N} - \overset{\circ}{O}: \qquad (D)$$

- (a) Which structures contain a positively charged carbon?
- (b) Which structures contain a positively charged nitrogen?

- (c) Which structures contain a positively charged oxygen?
- (d) Which structures contain a negatively charged carbon?
- (e) Which structures contain a negatively charged nitrogen?
- (f) Which structures contain a negatively charged oxygen?
- (g) Which structures are electrically neutral (contain equal numbers of positive and negative charges)? Are any of them cations? Anions?
- (h) Which structure is the most stable?
- (i) Which structure is the least stable?
- 10. Which resonance contributor makes the greater contribution to the resonance hybrid?





 CH_3

 CH_3











12. Are the following two structures resonance forms of one another?





13. The following is one way of writing the structure of the nitrate ion. Draw others.



WORK SHEET-1

1. Draw Resonance hybrid of following?



1. Draw the Resonating structure and Resonance Hybrid of following species?

S.No.	Compound	Resonating Structure
1.	H ₂ C ⁻ CH ₂	
2.	H ₃ C	
3.	NH ₂	
4.	CH-	
5.	NH ₂ O	
6.		
7.	CH ⁻	
8.	0	
9.	CH ₃ I O	



1. Draw the Resonating structure and Resonance Hybrid of following species?

S.No.	Compound	Resonating Structure
1.	CH•	
2.	CH•	
3.	CH	
4.	HC	
5.	H ₂ C CH [•] CH ₃	
6.		
7.	H ₂ C CH ₃	
8.	H ₂ C=O	

WORK SHEET-5

S.No.	Compound	Resonating Structure
1.	CH ⁺	
2.		



S.No.	Resonting Structure	Relative stability
1.	OCH_3 $\oplus O-CH_3$; $\oplus O$	
2.		
3.	$CH_3 - C - OH, CH_3 - C - OH, CH_3$	
4.	$\stackrel{NH_2}{\longmapsto} ; \stackrel{\stackrel{\oplus}{\longrightarrow}}{\longmapsto} ; \stackrel{\stackrel{\oplus}{\longrightarrow}}{\underset{\ominus}{\bigoplus}}$	
5.	$0 = C = 0; {}^{\oplus}0 \equiv C - 0^{\ominus}; 0 = C^{\oplus} - 0^{\ominus}; 0^{\ominus} - C^{\ominus} - 0^{\ominus}$	
6.	$\begin{array}{c} O \\ \parallel \\ H-O-C-NH_2; H-O=C-NH_2; H-O-C=NH_2; H-O-C-NH_2 \end{array} \\ \end{array} \\ \begin{array}{c} O \\ \downarrow \\ \oplus \\ H-O-C-NH_2; H-O-C-NH_2; H-O-C-NH_2 \end{array} \\ \end{array} \\ \begin{array}{c} O \\ \downarrow \\ \oplus \\ H-O-C-NH_2; H-O-C-NH_2 \end{array} \\ \begin{array}{c} O \\ \downarrow \\ \oplus \\ H-O-C-NH_2 \end{array} \\ \begin{array}{c} O \\ \downarrow \\ \oplus \\ H-O-C-NH_2 \end{array} \\ \begin{array}{c} O \\ \downarrow \\ \oplus \\ H-O-C-NH_2 \end{array} \\ \begin{array}{c} O \\ \downarrow \\ \oplus \\ H-O-C-NH_2 \end{array} \\ \begin{array}{c} O \\ \downarrow \\ \oplus \\ H-O-C-NH_2 \end{array} \\ \begin{array}{c} O \\ \downarrow \\ \oplus \\ H-O-C-NH_2 \end{array} \\ \begin{array}{c} O \\ \downarrow \\ \oplus \\ H-O-C-NH_2 \end{array} \\ \begin{array}{c} O \\ \downarrow \\ \oplus \\ H-O-C-NH_2 \end{array} \\ \begin{array}{c} O \\ \downarrow \\ \oplus \\ H-O-C-NH_2 \end{array} \\ \begin{array}{c} O \\ \downarrow \\ H-O-C-NH_2 \end{array} \\ \begin{array}{c} O \\ \downarrow \\ \oplus \\ H-O-C-NH_2 \end{array} \\ \begin{array}{c} O \\ \downarrow \\ \oplus \\ H-O-C-NH_2 \end{array} \\ \begin{array}{c} O \\ \downarrow \\ \oplus \\ H-O-C-NH_2 \end{array} \\ \begin{array}{c} O \\ \downarrow \\ H-O-C-NH_2 \end{array} \\ \begin{array}{c} O \\ H-O-NH_2 \end{array} \\ \begin{array}{c} O \\ H-O-C-NH_2 \end{array} \\ \\ \begin{array}{c} O \\ H-O-C-NH_2 \end{array} \\ \\ \begin{array}{c} O \\ H-O-C-NH_2 \end{array} \\ \end{array} $ \\ \begin{array}{c} O \\ H-O-C-NH_2 \end{array} \\ \begin{array}{c} O \\ H-O-C-NH_2 \end{array} \\ \\ \begin{array}{c} O \\ H-O-C-NH_2 \end{array} \\ \\ \end{array} \\ \begin{array}{c} O \\ H-O-C-NH_2 \end{array} \\ \\ \end{array} \\ \begin{array}{c} O \\ H-O-C-NH_2 \end{array} \\ \\ \end{array} \\ \begin{array}{c} O \\ H-O-C-NH_2 \end{array} \\ \\ \end{array} \\ \begin{array}{c} O \\ H-O-C-NH_2 \end{array} \\ \\ \end{array} \\ \\ \end{array} \\ \\ \end{array} \\ \begin{array}{c} O \\ H-O-C-NH_2 \end{array} \\ \\ \\ \end{array} \\ \\ \\ \end{array} \\ \\ \end{array} \\ \\ \end{array} \\ \\ \\ \end{array} \\ \\ \\ \end{array} \\ \\ \\ \\	



SUBJECTIVE TYPE QUESTIONS

1. How extensive are the conjugated systems in these molecules?



podophyllotoxin

Purpose of the problem

A chance to develop more deeply into what is meant by conjugation.

Suggested solution

The -lactam has two clearly defined conjugating systems : the amide and the more extended unsaturated acid going right through to the sulfur atom. These are shown by curly arrows on the first diagram. These systems are joined by a single bonds so they really are one system : all the *p* orbitals on the ringed atoms in the second diagram are more or less parallel and all are conjugated.



Podophyllotoxin has the obvious two benzene rings and cyclic ester conjugation, shown by curly arrows on the first diagram. Each benzene ring has substituents with lone pairs shown on the second diagram so this molecule has no less than six lone pairs of electrons involved in extended conjugation. There are three separate conjugated systems shown in boxes on the second diagram.



Answers

Single	Cho	ice Ques	tions													
1.	(C)	2.	(A)	3.	(D)	4.	(D)	5.	(A)	6	. (E)	7.	(A)	8.	(A)
9.	(A)	10.	(D)													
Sol.	(D)	(position o	Not R.	S. is change	d)											
11.	(C)															
Ans.	(C)															
Sol.	(A)		} ;₀	→ ◯	°O [⊕] I ⊂_O⊖			(E	3)) ←	$\rightarrow \Big($		` 0 [⊖]		
	(C)		ب	→ Bredťs viola	s rule			([ightarrow				
12.																

Ans. (C)

Sol. Strategy Two most dominating factors

(1) Number of bonds more Stability of R.S. more

(2) Atoms having complete octet Stability of R.S. more

Factors R.S.







19. (C)

Ans. 7





Ans. (a) Boron has six electrons in its outer shell in BCl₃ and can accommodate eithe electrons by having a B–Cl bond assume some double-bond character.



Sol. 20 atoms are conjugated.



9.

Ans. (a - D), (b - A, B), (c-None), (d-A), (e - None), (f-B, D), (g-A, B, D), (h-B), (i-C),

10.

11.

















