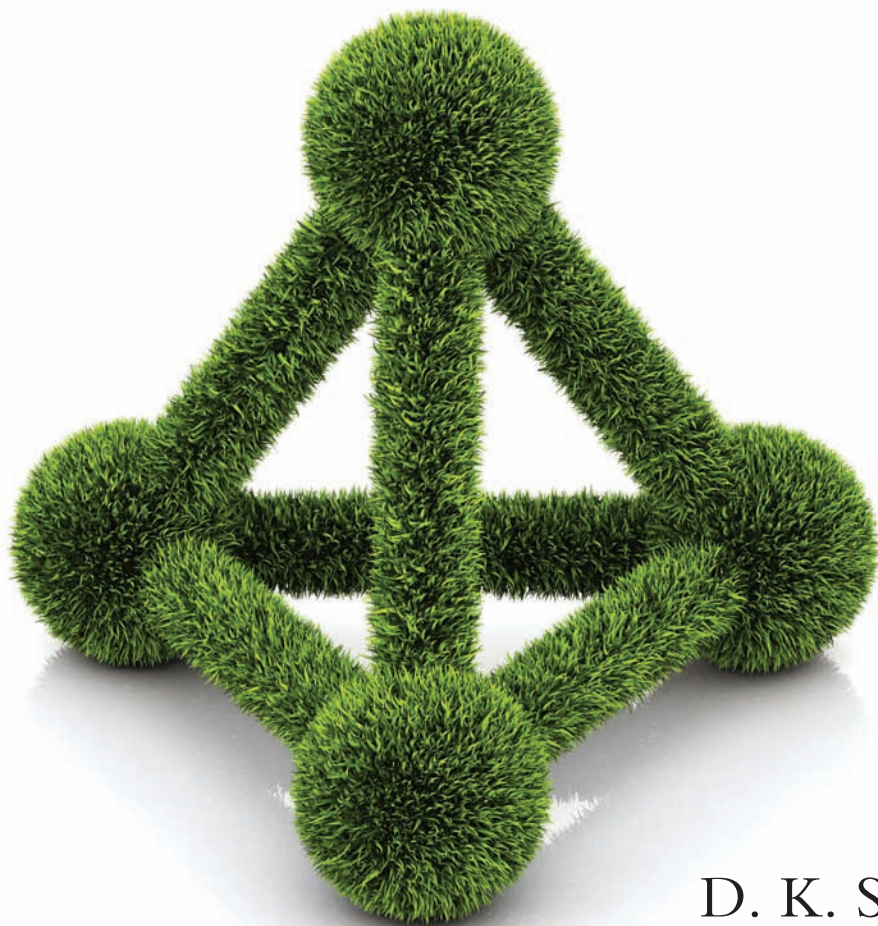


3rd edition

Conceptual Problems in

ORGANIC CHEMISTRY

for Engineering and Medical Entrance Examinations



D. K. Singh

Conceptual Problems in Organic Chemistry

[For Engineering and Medical Entrance Examinations]

Third Edition

D. K. SINGH

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To my mother, for her immense
love, patience and support

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Foreword

Chemistry is an ever-expanding branch of science that is based on well-established concepts. Most of the concepts are widely accepted and are often experimentally verified. Organic chemistry in particular deals with covalently linked carbon compounds. The stability of an organic compound in terms of its internal energy and rate of formation/decomposition can be predicted based on various physical concepts. A fair understanding of the possible involvement of intermediates and transient species and the kind of interaction among two or more reactants would enable us to propose a feasible reaction pathway.

Organic chemists have in their arsenal a plethora of reagents and conditions to carry out various synthetic transformations. Whether or not a reagent is suitable for a specific transformation can be predicted only through clear understanding of its reactivity. Man has developed various concepts on reactivity and selectivity by looking at mother nature. Her ability to generate numerous biomolecules that are indispensable to create and sustain life on earth has been a true inspiration to man. He cleverly applied those concepts in science and in everyday life.

Dr Singh has developed an invaluable resource based on concepts in organic chemistry for the benefit of students who are keen to learn more and prepare themselves for competitive examinations by intense problem solving. Enormous efforts have been expended for framing this extensive collection of single choice questions. Dr Singh took extraordinary care to ensure that questions with different levels of difficulty are included in order to keep the students of all levels interested in the subject. This unique collection of diverse questions enables the students to examine their own comprehension, conceptual understanding, logical and analytical thinking as well as time management skills. This book is far superior to many other national level competitive examination guides. The coverage of the subject is so exhaustive that the students would find every question a learning experience and say good bye to many guide books/question banks that contain monotonous questions. This is primarily due to Dr Singh's penchant for physical organic chemistry. He is well aware that understanding of theoretical, mechanistic and stereochemical concepts in organic chemistry is absolutely necessary to logically tackle even synthetic puzzles.

I am certain that a student who succeeds in answering most of Dr Singh's questions will be one of the top ranking students in the national level competitive examinations for undergraduate admission. I consider this book as an outstanding aid and recommend it wholeheartedly to those aspiring for admission to leading higher education institutions. This book would be an excellent reference book for postgraduate students and teachers as well.

Irishi N.N. Namboothiri
Professor
Department of Chemistry
Indian Institute of Technology Bombay
Mumbai 400 076

15 March 2013

Preface to the Third Edition

Organic Chemistry is not a formative science. It requires an interest in the nature and reaction of molecules. In other words, realization is the best way to learn organic chemistry because most of the problems are based on application of concepts. Therefore, students should have a clear concept of the subject and then learn to apply those concepts in solving problems. While formulating and designing the questions for this book, I had to consider all angles of each topic included in the syllabus. This book effectively catalyses the process of learning the subject. In fact, questions are designed to encourage students to learn more and more of Organic Chemistry. The third edition has been updated and now includes three new chapters on carbonyl compounds, ethers and amines, aromatic compounds and biomolecules. I am sure students will find this useful.

I extend my sincere thanks to Mr. Mohammad Ashfaq for his valuable feedback and suggestions.

I will appreciate your invaluable suggestions and feedback to improve future editions of this book.

D. K. Singh



About the Author

Devendra Kaumar Singh trains students appearing for the medical and engineering entrance examinations in an institute in Patna. He did his post-graduation from the B R Ambedkar Bihar University in Muzaffarpur, Bihar, and received his doctorate in 1991 from the Indian Institute of Science Bangalore, under the supervision of Professor S. N. Balasubrahmanyam. Following this, he worked as a post-doctoral fellow first with Professor Uday Maitra in the same institute for two years (1991–1993), and then with Professor R. C. Corcoran in the University of Wyoming, USA, for one year (1993–1994).

Dr Singh's research interest lies in the area of Physical Organic Chemistry. He has published three research papers in the *Bulletin of the Chemical Society of Japan*, *Indian Journal of Chemistry* and the *Journal of Organic Chemistry*, respectively.

Chapter

1





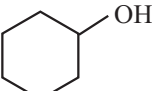
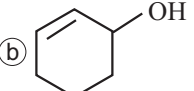
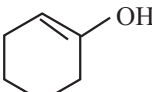
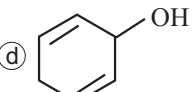

**Hybridization,
Resonance and
Aromaticity**



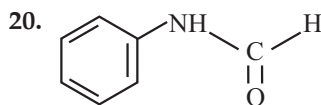
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Question Bank

- For exhibiting tetravalency, carbon atoms have to be excited. Now, which of the following statements is true?
 - Excitation occurs before bonding
 - Bonding occurs before excitation
 - Both bonding and excitation occur simultaneously
 - Two bonds are formed first, then excitation occurs followed by formation of another two bonds
- Bond formation is
 - always exothermic
 - always endothermic
 - neither exothermic nor endothermic
 - sometimes exothermic and sometimes endothermic
- Which of the following statements is true about bonding and excitation?
 - Energy required for excitation of carbon atoms (96 Kcal/mol) is less than energy released in bonding
 - Energy required for excitation is more than energy released in bonding
 - Energy required for excitation is equal to the energy released in bonding
 - None of these
- Which of the following statements is true about hybridization?
 - Only those atomic orbitals can be hybridized which do not differ much in shape.
 - Only those atomic orbitals can be hybridized which do not differ much in energy.
 - Only those atomic orbitals can be hybridized which do not differ much in size.
 - Only those atomic orbitals can be hybridized which do not differ much in overlap integrals.
- Which of the following statements is true about hybridization?
 - Hybridization generates new set of atomic orbitals identical in shape but not in size and energy.
 - Hybridization generates new set of atomic orbitals identical in size but not in shape and energy.
 - Hybridization generates new set of atomic orbitals identical in energy but not in shape and size.
 - Hybridization generates new set of atomic orbitals identical in shape, size and energy.
- Which of the following statements is true about hybridization?
 - Hybrid orbitals frequently undergo linear overlaps making sigma bonds.
 - Hybrid orbitals frequently undergo lateral overlaps making π -bonds. In other words, there are several compounds in which π -bonds are formed using hybrid orbitals.
 - Hybrid orbitals are molecular orbitals.
 - A hybrid orbital bigger in size makes shorter bond.
- In $2sp$ hybridization, $2s$ -orbital can be mixed with
 - Only $2p_x$
 - Only $2p_y$
 - Only $2p_z$
 - Any one of $2p_x$, $2p_y$ and $2p_z$
- In $2sp^2$ orbital, character of $2p_z$ orbital will be
 - always 33.33%
 - always 0%
 - always 66.66%
 - either 33.33 % or 0 %

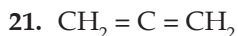
9. In $2sp^3$ orbital
- characters of $2p_x$, $2p_y$ and $2p_z$ orbitals are equal to each other but less than that of $2s$ -orbital
 - characters of $2p_x$, $2p_y$ and $2p_z$ orbitals are equal to each other but more than that of $2s$
 - characters of $2s$, $2p_x$, $2p_y$ and $2p_z$ orbitals are equal to each other
 - characters of $2p_x$, $2p_y$ and $2p_z$ are not equal to each other
10. Which of the following statements about the energy of hybrid orbitals resulting from mixing of $2s$ and $2p$ orbitals is true?
- $E_{2p} > E_{sp^3} > E_{sp^2} > E_{sp} > E_{2s}$
 - $E_{sp^3} > E_{sp^2} > E_{sp} > E_{2p} > E_{2s}$
 - $E_{2p} > E_{sp} > E_{sp^2} > E_{sp^3} > E_{2s}$
 - $E_{2p} > E_{sp} > E_{2s} > E_{sp^2} > E_{sp^3}$
11. Which of the following statements about the size of hybrid orbitals resulting from mixing of $2s$ and $2p$ orbitals is true?
- $2s > 2p > sp^3 > sp^2 > sp$
 - $2p > 2s > sp^3 > sp^2 > sp$
 - $2p > sp^3 > sp^2 > sp > 2s$
 - $sp^3 > sp^2 > sp > 2p > 2s$
12. Shapes of sp^3 , sp^2 and sp orbitals are like
- 
 - 
 - 
 - 
13. Which of following statements about overlap integrals of the various orbitals is true?
- $2p > 2s > 2sp^3 > 2sp^2 > 2sp$
 - $2p > 2sp^3 > 2sp^2 > 2sp > 2s$
 - $2p > 2sp > 2sp^2 > 2sp^3 > 2s$
 - $2sp^3 > 2sp^2 > 2sp > 2p > 2s$
14. Energy content of a molecule will be less if
- bond energy is more
 - bond energy is less
 - magnitude of overlap is very less
 - none of these
15. Which of the following orders is correct for electronegativity?
- $sp^3C > sp^2C > spC$
 - $spC > sp^2C > sp^3C$
 - $sp^2C > spC > sp^3C$
 - $sp^3C > spC > sp^2C$
16. In which of the following compounds, C has used sp^2 orbital in making C–O bond?
- 
 - 
 - 
 - 
17. The orbitals used by C in forming C–H and C–Cl bonds of CH_2Cl_2 are
- four sp orbitals
 - four sp^2 orbitals
 - four sp^3 orbitals
 - none of these
18. $CH_2 = CH - CN$
 $\quad \quad \quad 3 \quad \quad 2 \quad \quad 1$
 Cl–C2 bond of this molecule is formed by
- sp^3 – sp^2 overlap
 - sp^2 – sp^3 overlap
 - sp^2 – sp overlap
 - sp^2 – sp^2 overlap
19. 
- In this molecule, there are two C–O bonds. Which of the following statements is true about these bonds?
- Both C–O bonds are formed by sp^3 – sp^3 overlaps
 - Both C–O bonds are formed by sp^2 – sp^2 overlaps

- (c) One C-O bond is formed by sp^2-sp^3 overlap while the other C-O bond is formed by sp^3-sp^3 overlap
 (d) Both C-O bonds are formed by sp^2-sp^3 overlaps



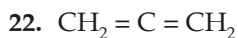
In this molecule,

- (a) both C-N bonds are formed by sp^2-sp^2 overlaps
 (b) one C-N bond is formed by sp^2-sp^2 overlap while the other by sp^2-sp^3 overlap
 (c) both C-N bonds are formed by sp^2-sp^3 overlaps
 (d) both C-N bonds are formed by sp^2-sp^2 overlaps

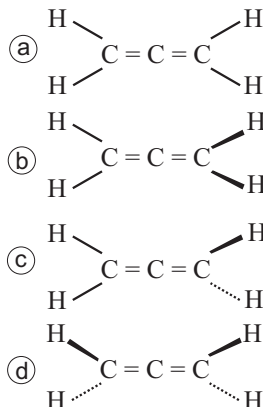


In this molecule (allene)

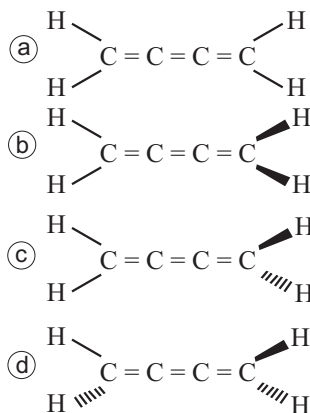
- (a) all three C-atoms are sp^2 hybridized
 (b) both terminal C-atoms are sp^2 hybridized while central C-atom is sp -hybridized
 (c) both terminal C-atoms are sp -hybridized while central C-atom is sp^2 hybridized
 (d) none of these



Which of the following structures is most appropriate for this molecule?

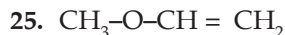


Which of the following structures is most appropriate for this molecule?



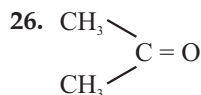
24. Which of the following compounds has maximum number of sp -hybridized C-atoms?

- (a) $(CN)_2$
 (b) $CH \equiv C-CN$
 (c) $HC \equiv C-CH_2-CH = C = C = CH_2$
 (d) $CH_2 = C = CH-CN$



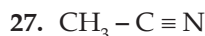
Oxygen atom of this molecule is

- (a) sp^3 hybridized
 (b) sp^2 hybridized
 (c) sp -hybridized
 (d) unhybridized



Oxygen atom of this molecule is

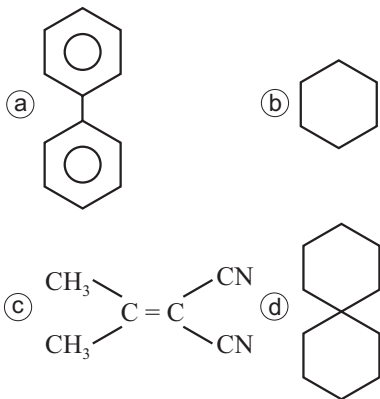
- (a) sp^3 -hybridized
 (b) sp^2 -hybridized
 (c) sp -hybridized
 (d) unhybridized



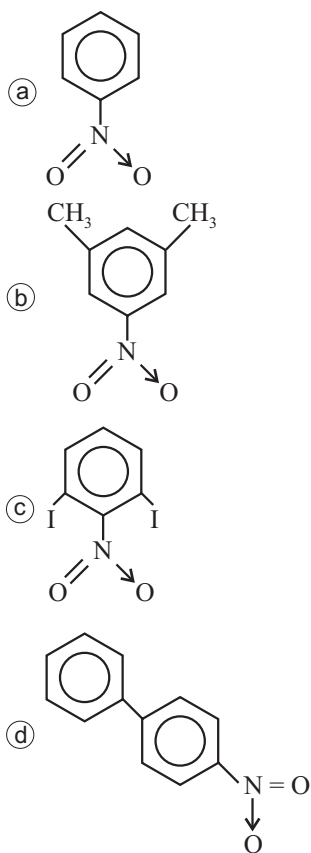
Nitrogen atom of this molecule is

- (a) sp^3 -hybridized (b) sp^2 -hybridized
 (c) sp -hybridized (d) unhybridized

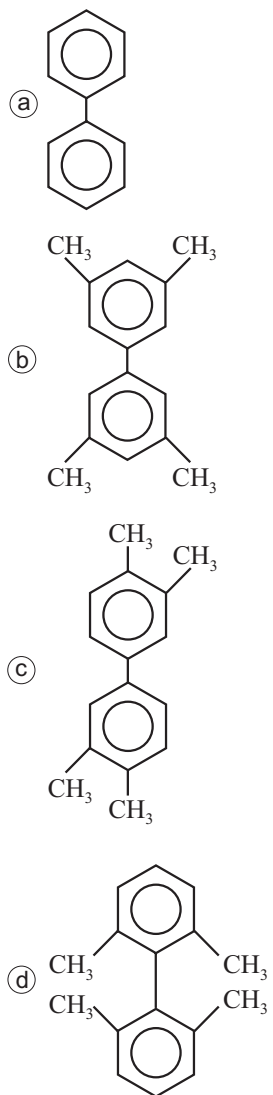
28. In which of the following molecules, all atoms are coplanar?



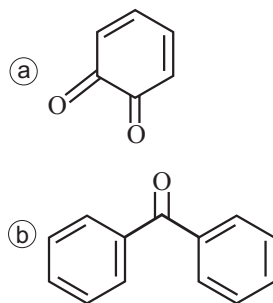
29. In which of the following molecules, $-\text{NO}_2$ group is not coplanar with phenyl ring?

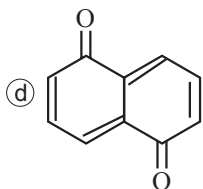
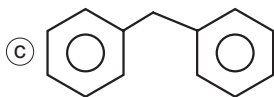


30. In which of the following molecules both phenyl rings are not coplanar?

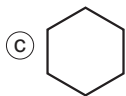
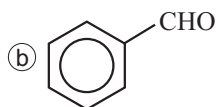
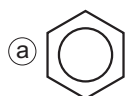


31. In which of the following molecules, all atoms are not coplanar?





32. In which of the following molecules, all bond angles are not similar?



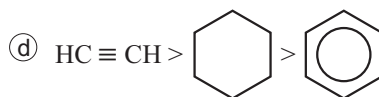
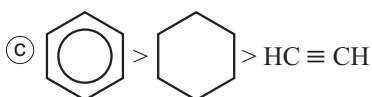
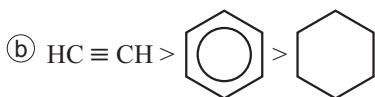
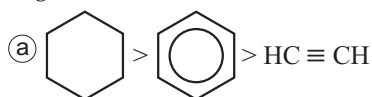
33. Which of the following is the correct order of bond angles?

- (a) $\text{NH}_3 > \text{H}_2\text{O} > \text{CH}_4$
 (b) $\text{H}_2\text{O} > \text{NH}_3 > \text{CH}_4$
 (c) $\text{CH}_4 > \text{NH}_3 > \text{H}_2\text{O}$
 (d) $\text{CH}_4 > \text{H}_2\text{O} > \text{NH}_3$

34. Which of the following is the correct order of bond angles?

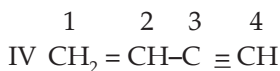
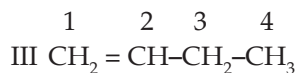
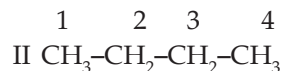
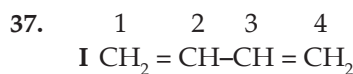
- (a) $\text{NH}_4^+ > \text{H}_3\text{O}^+ > \text{H}_2\text{O}$
 (b) $\text{H}_3\text{O}^+ > \text{NH}_4^+ > \text{H}_2\text{O}$
 (c) $\text{H}_2\text{O} > \text{H}_3\text{O}^+ > \text{NH}_4^+$
 (d) $\text{NH}_4^+ > \text{H}_2\text{O} > \text{H}_3\text{O}^+$

35. Which of the following order of bond angles is correct?



36. Which of the following orders of bond energy is correct?

- (a) $\text{C-C} > \text{N-N} > \text{O-O}$
 (b) $\text{O-O} > \text{N-N} > \text{C-C}$
 (c) $\text{N-N} > \text{C-C} > \text{O-O}$
 (d) $\text{C-C} > \text{O-O} > \text{N-N}$



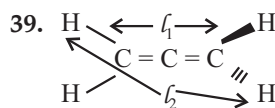
Which of the following is the correct order of C_2 - C_3 bond length?

- (a) $\text{II} > \text{I} > \text{III} > \text{IV}$ (b) $\text{II} > \text{III} > \text{I} > \text{IV}$
 (c) $\text{III} > \text{I} > \text{IV} > \text{II}$ (d) $\text{IV} > \text{I} > \text{III} > \text{II}$



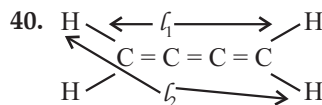
Which of the following is the correct order of C-C bond length among these compounds?

- (a) $\text{I} > \text{II} > \text{III}$ (b) $\text{III} > \text{II} > \text{I}$
 (c) $\text{III} > \text{I} > \text{II}$ (d) $\text{II} > \text{I} > \text{III}$



Which of the following is the correct order of spatial distances l_1 and l_2 ?

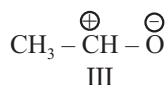
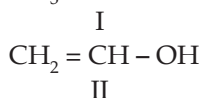
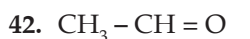
- (a) $l_1 = l_2$ (b) $l_1 > l_2$
 (c) $l_1 < l_2$ (d) $l_2 = 2l_1$



Which of the following is the correct order of spatial distances l_1 and l_2 ?

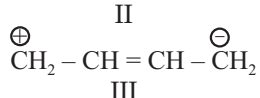
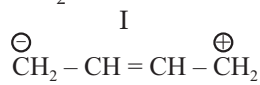
- (a) $l_1 = l_2$ (b) $l_1 > l_2$
 (c) $l_1 < l_2$ (d) $l_2 = 2l_1$

41. Resonance involves
 (a) change in the positions of atoms
 (b) change in the positions of both σ and π electrons
 (c) change in the positions of only π electrons
 (d) change in the positions of only σ electrons



Among these, which are canonical structures?

- (a) I and II (b) I and III
 (c) II and III (d) all



Among these which are canonical structures?

- (a) I and II (b) I and III
 (c) II and III (d) all of these

44. Which of the following statements is true?

- (a) Resonance is an intermolecular process
 (b) Canonical structures are imaginary
 (c) Canonical structures are real
 (d) A canonical structure explains all features of a molecule

45. For a resonating molecule, real structure is

- (a) the resonance hybrid
 (b) the canonical structures
 (c) sometimes resonance hybrid and sometimes canonical structures
 (d) none of these

46. A resonance hybrid is the one which is contributed by

- (a) all canonical structures
 (b) only the least stable canonical structure
 (c) only the most stable canonical structure
 (d) none of these

47. In the resonance hybrid

- (a) all canonical structures contribute equally
 (b) more stable canonical structure contributes more than less stable canonical structure
 (c) more stable canonical structure contributes less than less stable canonical structure
 (d) there is no contribution of any canonical structure

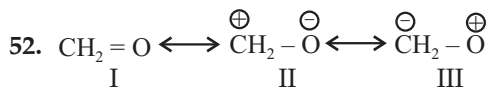
48. Delocalization of electrons increases molecular stability because

- (a) electrons-nuclei attraction increases
 (b) electrons-electrons repulsion increases
 (c) potential energy of the molecule increases
 (d) potential energy of the molecule remains unaffected

49. Resonance energy is

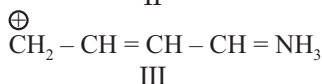
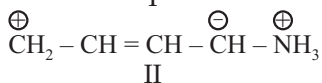
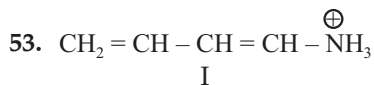
- (a) equal to the energy of resonance hybrid
 (b) equal to the energy of most stable canonical structure
 (c) equal to the energy of least stable canonical structure
 (d) equal to the difference in energies of the most stable canonical structure and resonance hybrid

50. Resonance energy is
- stored in the molecule
 - released by the molecule
 - neither stored nor released by the molecule
 - sometimes stored and sometimes released by the molecule
51. All canonical structures of a molecule
- must have different number of unpaired electrons
 - must have different number of paired electrons
 - must be always equivalent
 - need not be always equivalent but they should not differ much in stability



Which of these structures is practically not a valid canonical structure of formaldehyde?

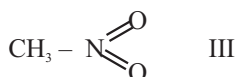
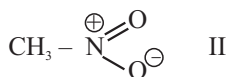
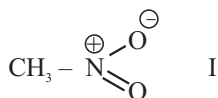
- I
- II
- III
- none of these



Which of these structures is not a valid canonical structure?

- I
- II
- III
- none of these

54.



Which of these structures is not a valid canonical structure of nitromethane?

- I
- II
- III
- none of these

55. A canonical structure will be more stable if

- it has more number of π -bonds than if it has less number of π -bonds
- it has charge separation than if it has no charge separation
- it has greater length of charge separation than if it has lower length of charge-separation
- it has positive charge on more electronegative atom than if it has positive charge on less electronegative atom

56. Which of the following statements is true about the contributions of canonical structures in the resonance hybrid?

- A charge-separated canonical structure contributes more than a canonical structure without charge-separation
- A canonical structure with less number of π bonds contributes more than a canonical structure with more number of π bonds
- A canonical structure with negative charge on less electronegative atom contributes more than a canonical structure with negative charge on more electronegative atom
- contribution of a charge-separated canonical structure will be more in a polar solvent than in a non-polar solvent

57.

