AROMATICITY

Peter Sykes

ETGT CHEMISTRY CASSETTE

CHEMISTRY CASSETTES

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USING THIS CHEMISTRY CASSETTE

Please read this before you start.

This Chemistry Cassette learning programme has two components — an audio-cassette and this workbook. They are designed to be used together, so make sure that you have both of them before you start. The cassette will fit any standard audio-cassette player. You will have to turn it over to side B about half-way through the programme.

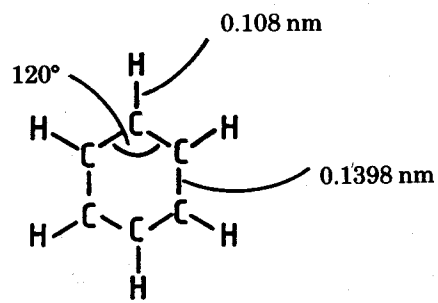
During the course of the programme you will, from time to time, be asked to ***stop the tape*** and answer questions — so have pencil and paper ready before you begin to listen. You will also be referred regularly to the reaction schemes in this workbook; each of these is numbered and you will be given the appropriate number whenever you need to locate a particular scheme. As the answers to some of the questions are given in subsequent schemes use a card or piece of paper to cover those beyond the one currently being referred to.

The whole point of this type of presentation is that you should be able to follow it at a rate that suits *you*. Don't hesitate, therefore, to stop the tape if you want to think about something, to consider a reaction scheme in detail, to refer back to a previous scheme, or for any other reason. Equally, don't hesitate to turn the tape back, using the re-wind control, if there's a section that you haven't understood properly, or that you would like to go over again

Running times:
Side A. 48 mins.
Side B. 50 mins..

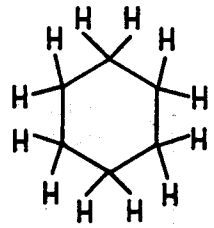
AROMATICITY

1

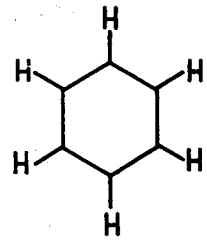


BENZENE : SHAPE AND DIMENSIONS

2



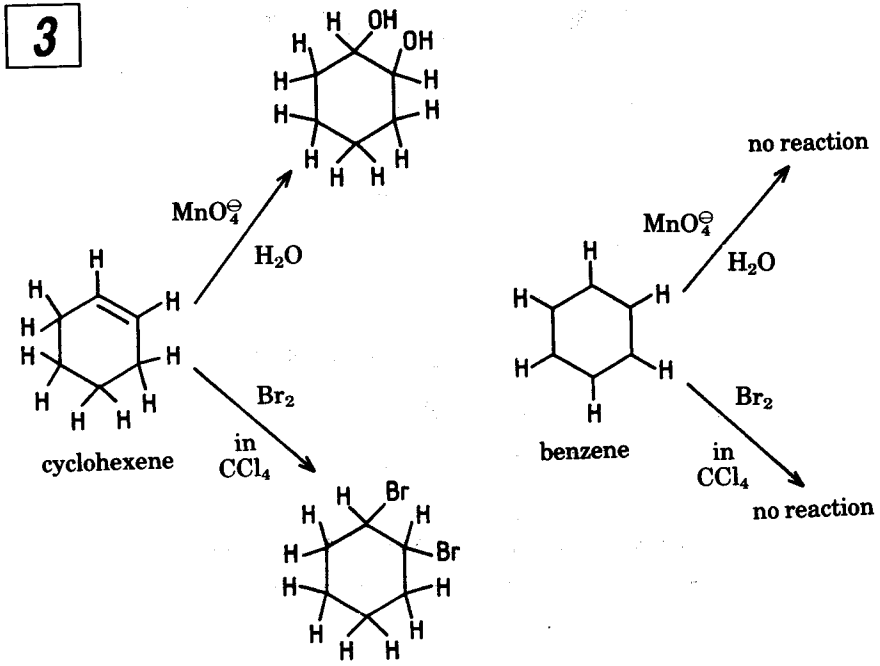
cyclohexane: C_6H_{12}
saturated



benzene: C_6H_6
unsaturated

CYCLOHEXANE / BENZENE COMPARISON

3



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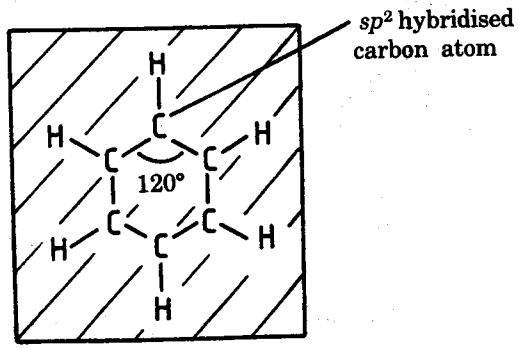
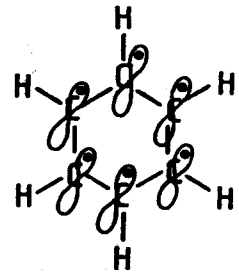
TESTS FOR UNSATURATION



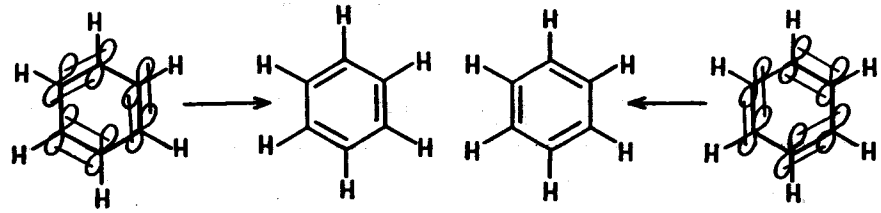
BENZENE: FLAT, REGULAR HEXAGON

5



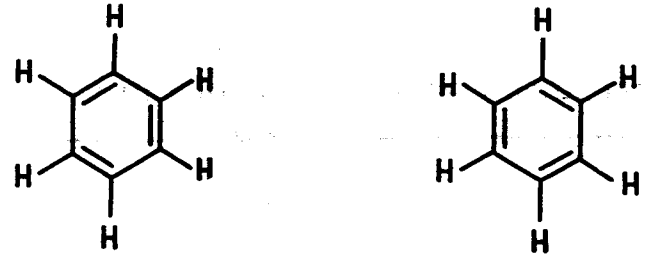
BENZENE : SIX *p* ATOMIC ORBITALS

6



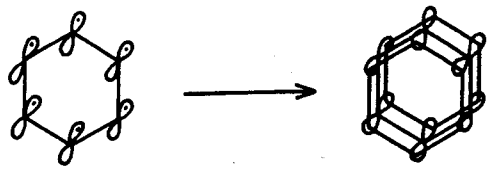
ADJACENT OVERLAP ⟶ KEKULE STRUCTURES

7



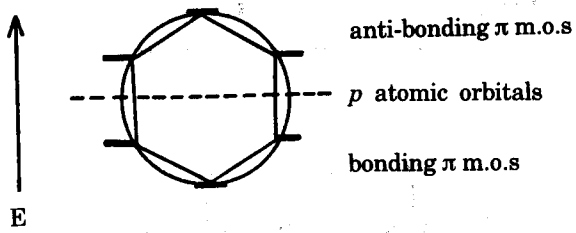
KEKULE STRUCTURES: IRREGULAR HEXAGONS

8



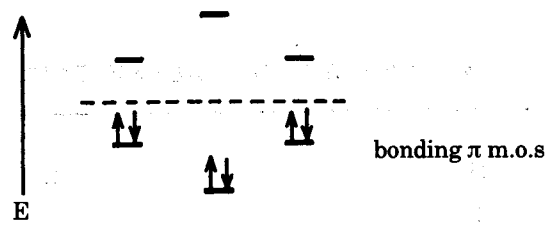
"ALL ROUND" OVERLAP OF *p* ORBITALS

9



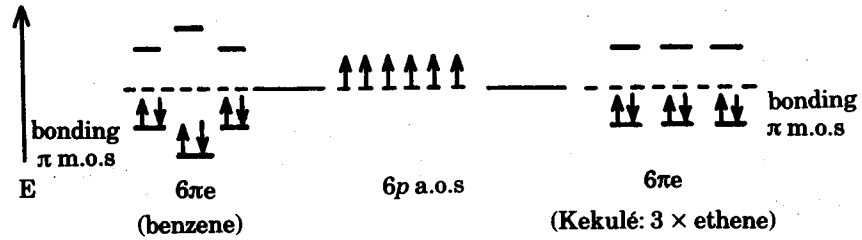
FROST AND MUSULIN POLYGON: BENZENE

10



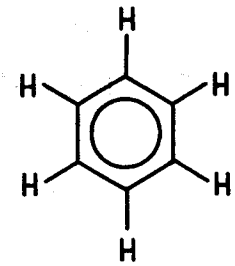
BENZENE: ELECTRON ALLOCATION TO M.O.s

11



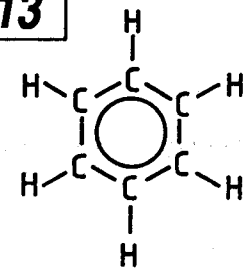
ELECTRON ALLOCATION: BENZENE vs. 3 × ETHENE

12

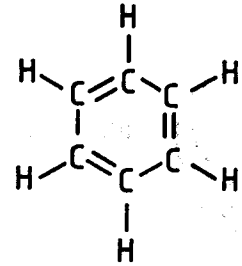


BENZENE: CURRENT REPRESENTATION

13



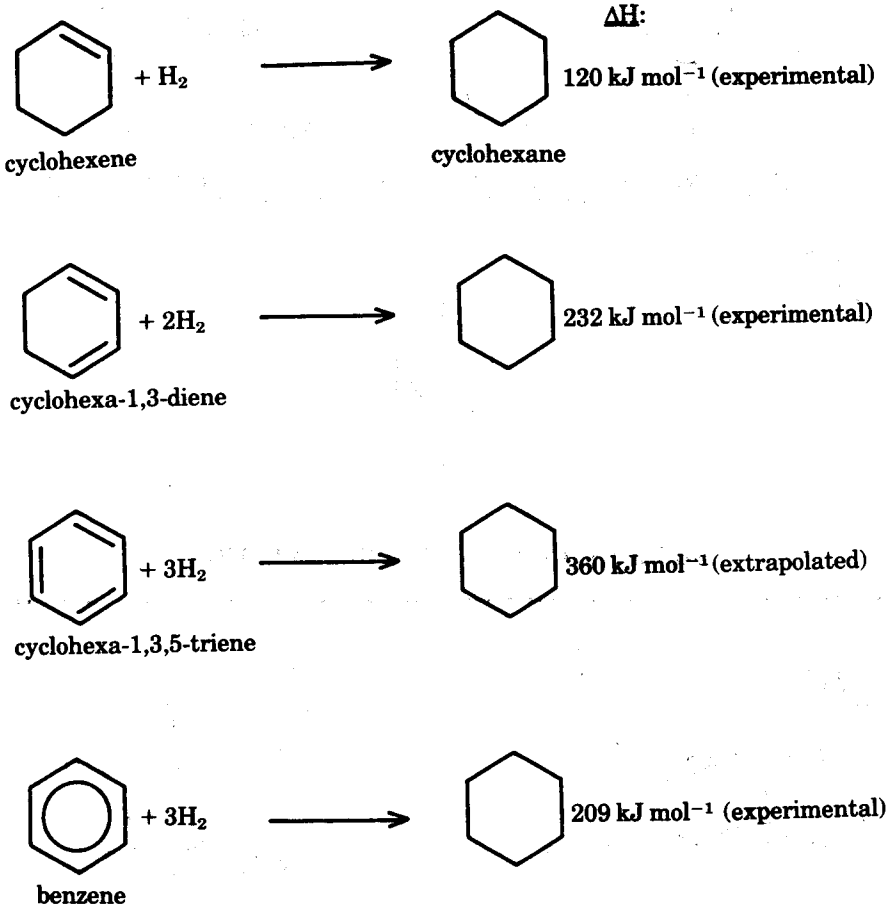
"real" benzene:
3299 kJ mol^{-1} (expt.)



Kekulé structure:
3449 kJ mol^{-1} (calc.)

HEAT OF COMBUSTION DATA

14



HEAT OF HYDROGENATION DATA

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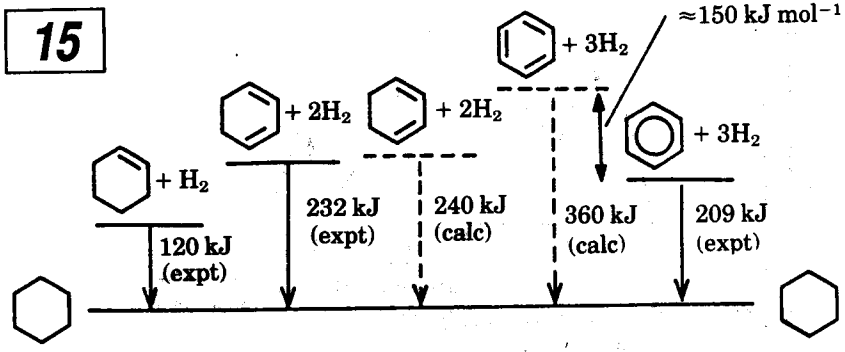

HYDROGENATION DATA: GRAPHICAL SUMMARY

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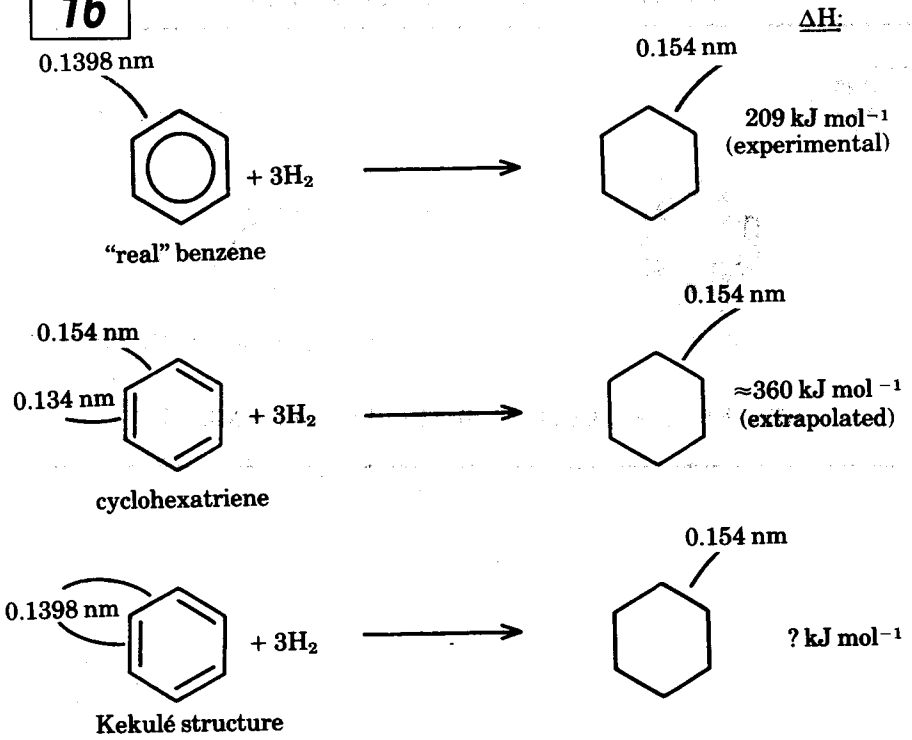
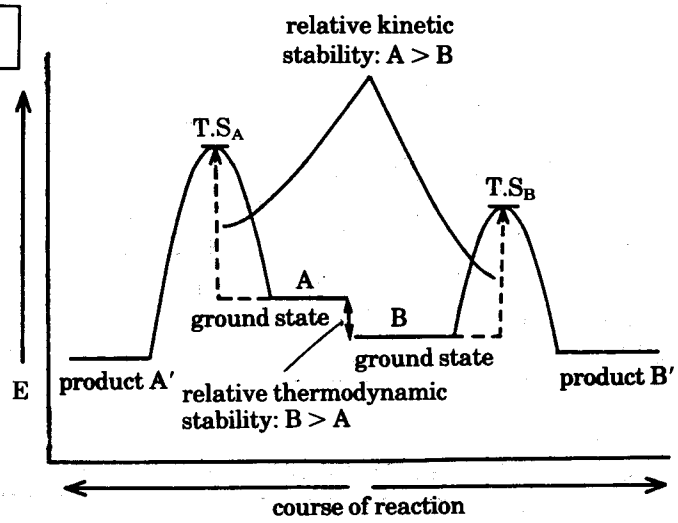


VALIDITY OF HYDROGENATION DATA

17



THERMODYNAMIC vs. KINETIC STABILITY

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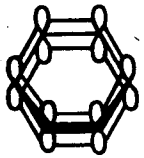
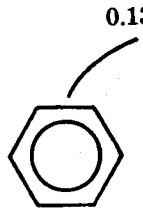


planarity



all C–C bond lengths the same

BENZENE: "AROMATIC" SHAPE AND DIMENSIONS

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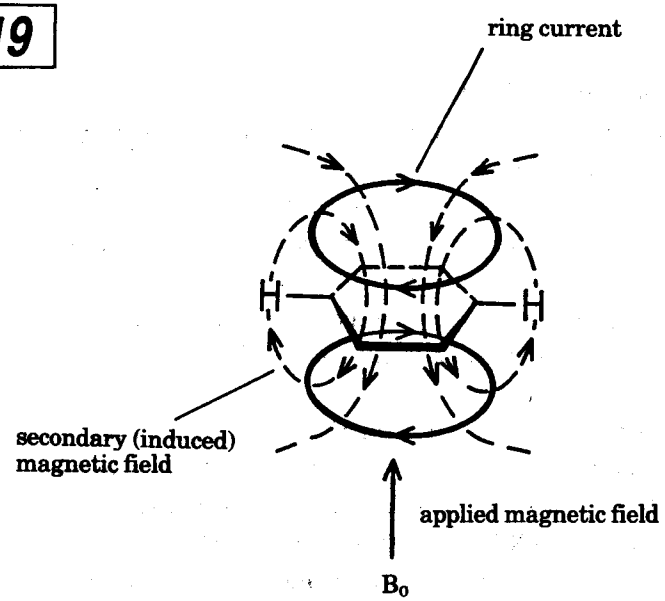
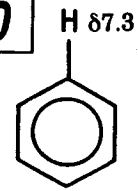
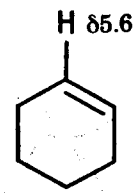


N.M.R. SPECTROSCOPY: AROMATIC RING CURRENT

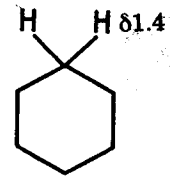
20



benzene



cyclohexene



cyclohexane

COMPARISON OF PROTON CHEMICAL SHIFTS (δ)

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1) THERMODYNAMIC STABILITY

Data from heats of combustion and hydrogenation provide information about ground state of molecule: relatively useful.

2) KINETIC STABILITY AND REACTION TYPE

The former involves a transition state as well as the ground state, and is relatively unreliable.

Substitution by electrophiles, rather than the addition which might have been expected, is potentially more useful.

3) MOLECULAR GEOMETRY

Data from X-ray diffraction, etc. Planarity, bond length values intermediate between C=C and C–C, and non-alternating. Gives basic information about whether molecule is "benzene-like".

4) RING CURRENTS AND N.M.R. PROTON CHEMICAL SHIFTS.

Chemical shift data extremely easy to obtain; is very useful and relatively reliable.

CRITERIA FOR AROMATIC CHARACTER: SUMMARY

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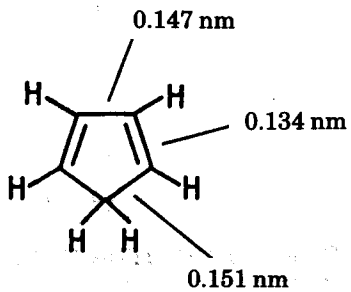

CYCLOPENTA-1,3-DIENE

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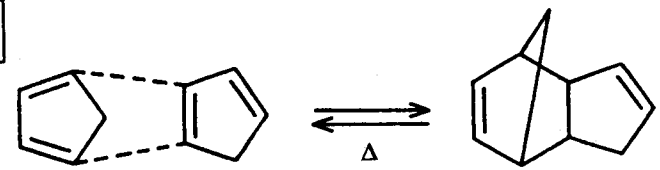

dicyclopentadiene

CYCLOPENTADIENE: DIMERISATION

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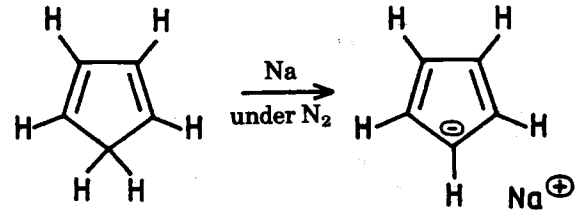
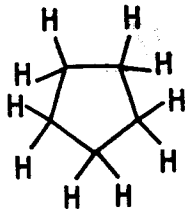


cyclopentadiene
$pK_a \approx 15$

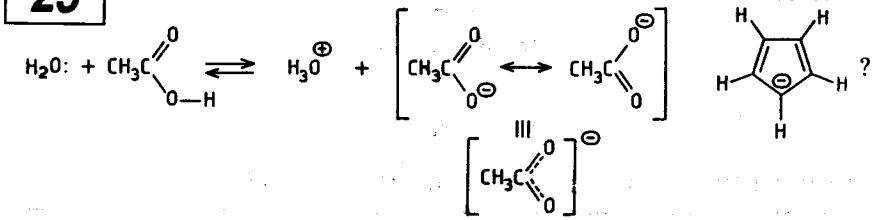
cf.



cyclopentane
$pK_a \approx 40$

CYCLOPENTADIENE: ACIDITY (pK_a) vs. CYCLOPENTANE

25



ETHANOIC ACID: ACIDITY AND ANION STABILISATION

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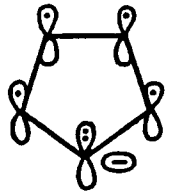

CYCLOPENTADIENYL ANION: *p* ORBITALS

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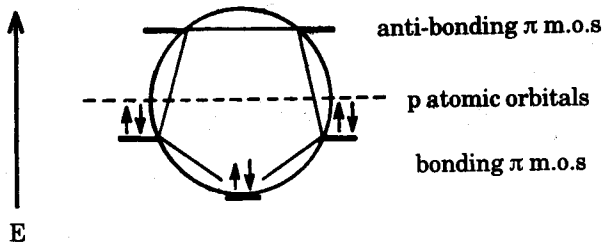

CYCLOPENTADIENYL ANION: FROST AND MUSULIN POLYGON

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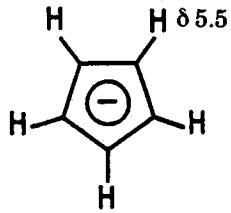

CYCLOPENTADIENYL ANION : REPRESENTATION AND δ VALUE

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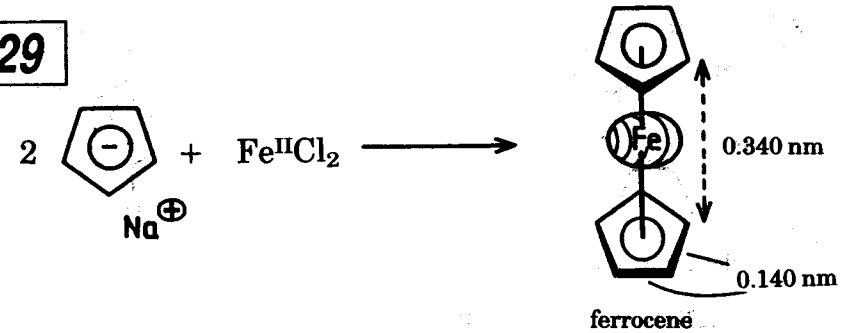

FERROCENE: PREPARATION AND DIMENSIONS

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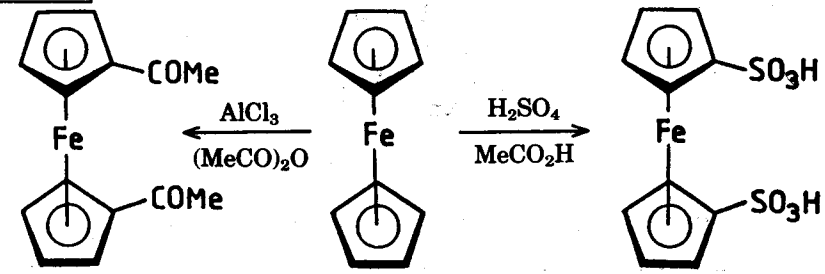

FERROCENE: F. C. ACYLATION AND SULPHONATION

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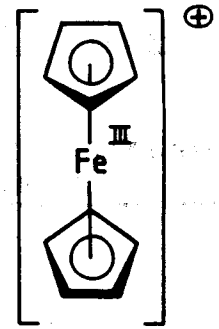

FERRICENIUM CATION

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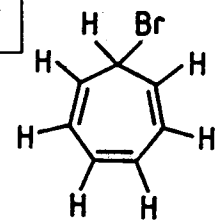
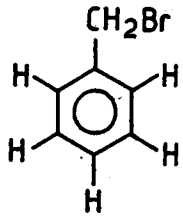


cycloheptatrienyl bromide



benzyl bromide

ISOMERIC CYCLOHEPTATRIENYL (TROPYLIUM) AND BENZYL BROMIDES

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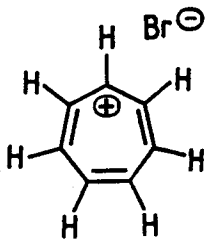

CYCLOHEPTATRIENYL BROMIDE: ION PAIR

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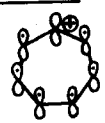

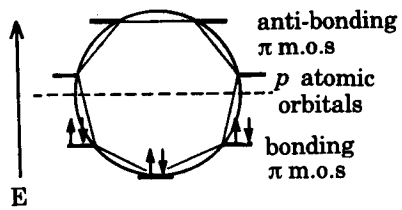

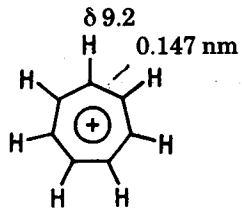

CYCLOHEPTATRIENYL CATION: FROST AND MUSULIN POLYGON AND DIMENSIONS

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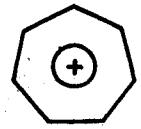
cyclopentadienyl anion

benzene



cycloheptatrienyl cation

COMPARISON OF STRUCTURAL REPRESENTATIONS

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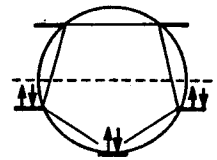
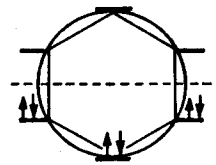
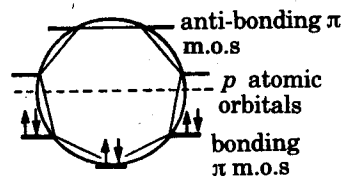


cyclopentadienyl anion



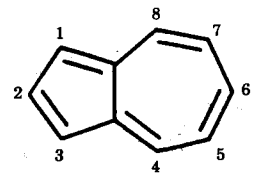
benzene



cycloheptatrienyl cation

COMPARISON OF F. AND M. POLYGONS: ALL BONDING M.O.s FILLED

37



AZULENE

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AZULENE: *p* ORBITAL OVERLAP

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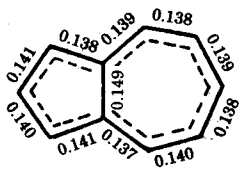
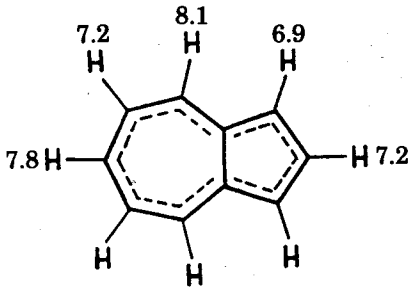


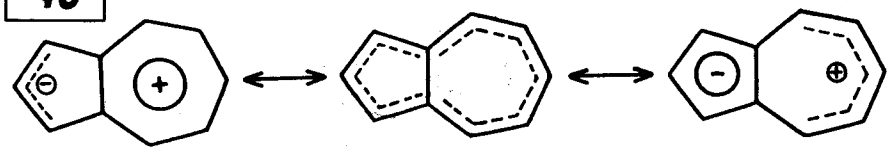
bond lengths (nm)



δ values

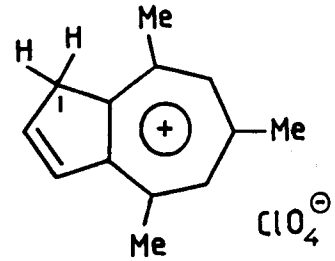
AZULENE: DIMENSIONS AND δ VALUES

40



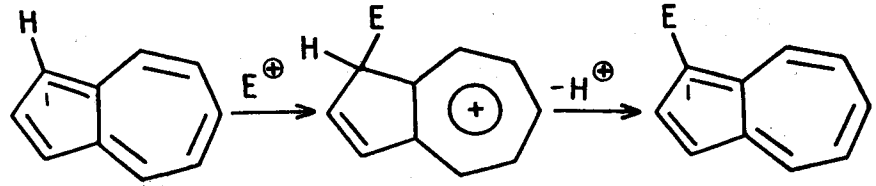
AZULENE: DIPOLAR CHARACTER?

41



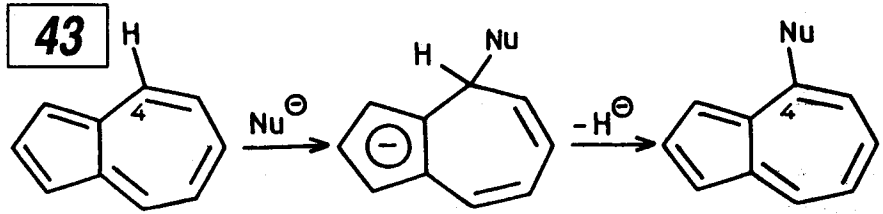
AZULENE: PROTONATION OF A DERIVATIVE

42



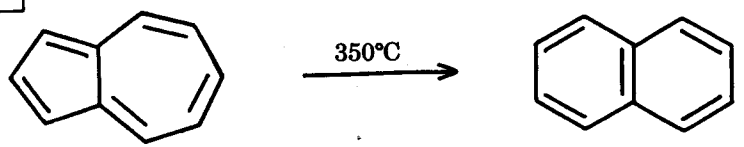
AZULENE: ELECTROPHILIC SUBSTITUTION

43



AZULENE: NUCLEOPHILIC SUBSTITUTION

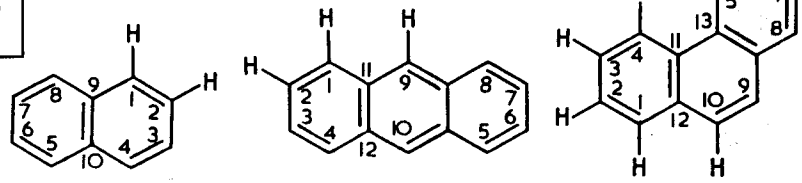
44



azulene naphthalene

AZULENE: ISOMERISATION TO NAPHTHALENE

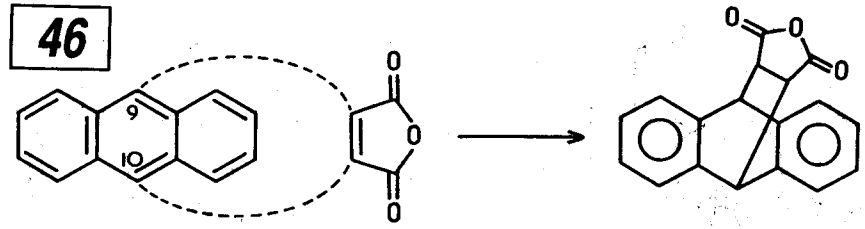
45



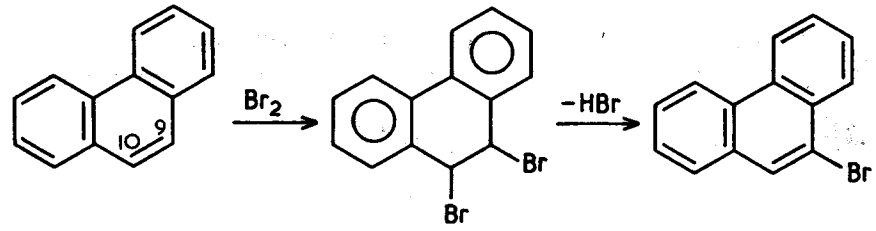
	Naphthalene	Anthracene	Phenanthrene
C—C bond lengths: (nm)	1,2 0.136 2,3 0.142 1,9 0.142 9,10 0.142	1,2 0.137 2,3 0.141 1,11 0.140 9,11 0.140 11,12 0.144	1,2 0.138 2,3 0.140 3,4 0.138 4,11 0.141 11,12 0.140 12,1 0.146 12,10 0.139 11,13 0.145 9,10 0.137
δ:	H^1 7.8 H^2 7.5	H^1 7.9 H^2 7.4 H^9 8.3	H^1 7.7 H^2 7.4 H^3 7.5 H^4 8.5 H^9 8.4
stabilisation energies ($kJ\ mol^{-1}$)	251	349	380

NAPHTHALENE, ANTHRACENE, PHENANTHRENE: PHYSICAL DATA

46



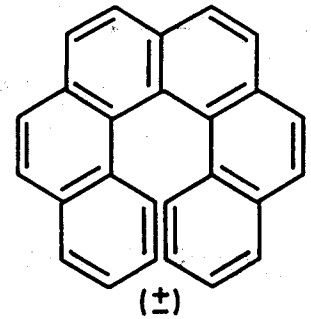
anthracene maleic anhydride Diels-Alder adduct



phenanthrene 9,10-dibromide 9-bromo

ANTHRACENE, PHENANTHRENE: DOUBLE BOND CHARACTER

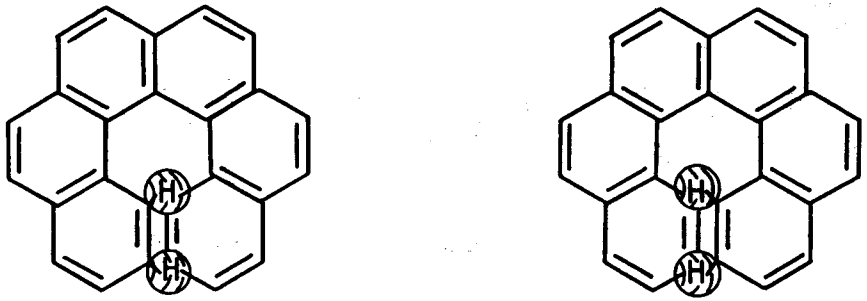
47



(±)

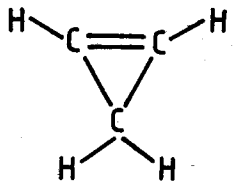
26 π ELECTRON HEXACYCLIC SYSTEM: CHIRAL

48



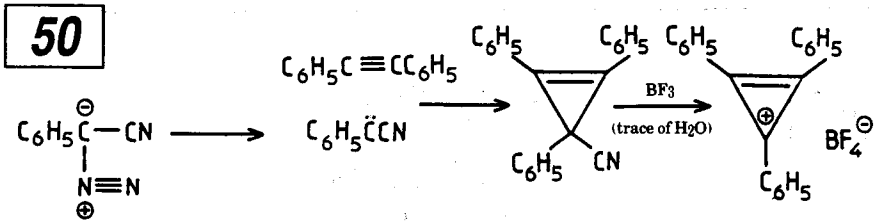
HEXAHELICENE: STRUCTURE OF MIRROR IMAGES

49



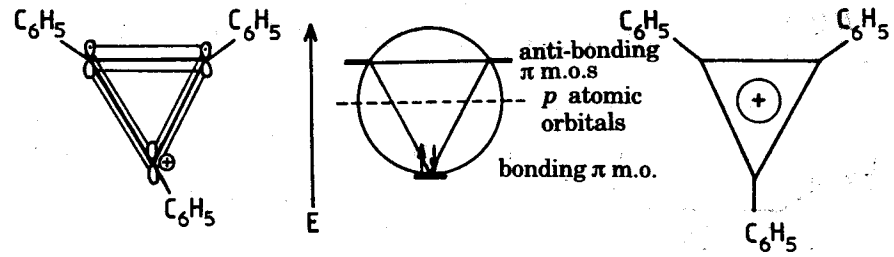
CYCLOPROPENE

50



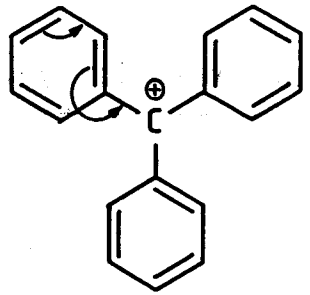
SUBSTITUTED CYCLOPROPENE AND CYCLOPROPENYL CATION: PREPARATION

51



CYCLOPROPENYL CATION: F. AND M. POLYGON

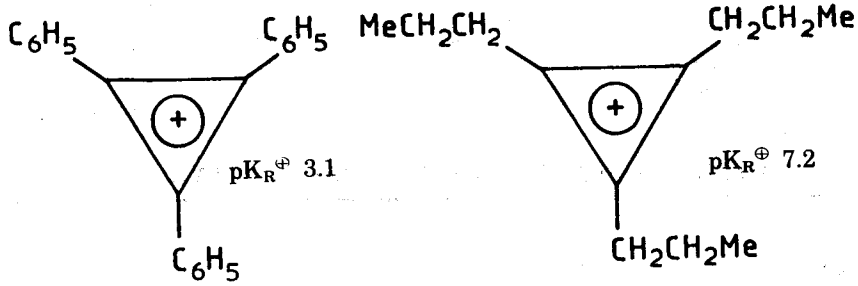
52



TRIPHENYLMETHYL CATION

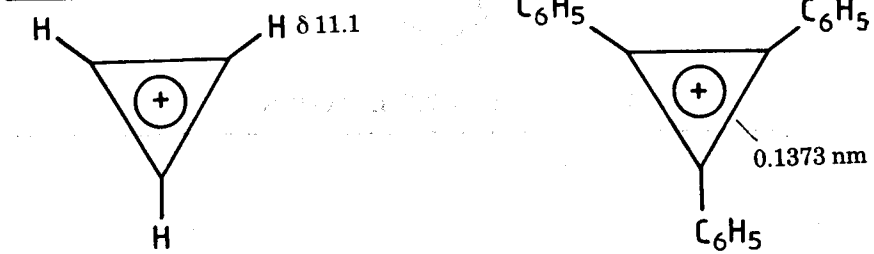
53

$$R^{\oplus} + 2H_2O \overset{K_R^{\oplus}}{\rightleftarrows} R\text{-}OH + H_3O^{\oplus}$$



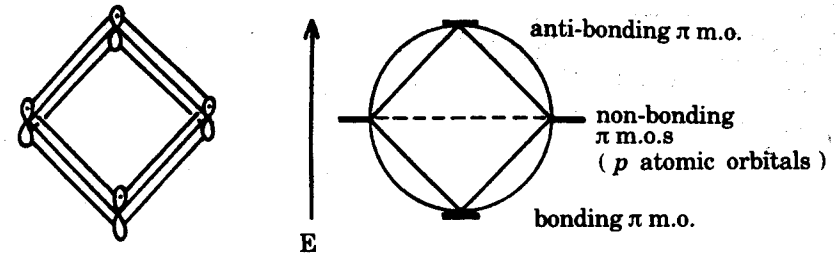
CYCLOPROPENYL CATIONS: $pK_R^{\oplus}$ VALUES

54



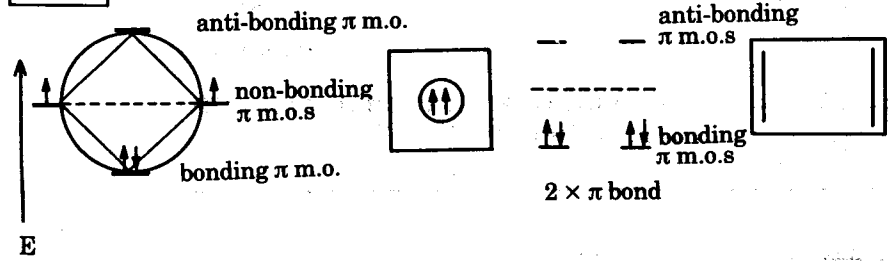
CYCLOPROPENYL CATIONS: PHYSICAL DATA

55



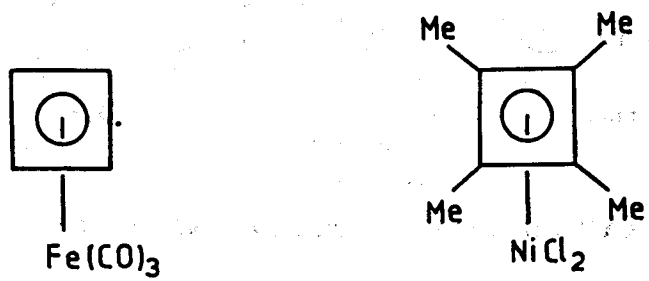
CYCLOBUTADIENE: F. AND M. POLYGON

56



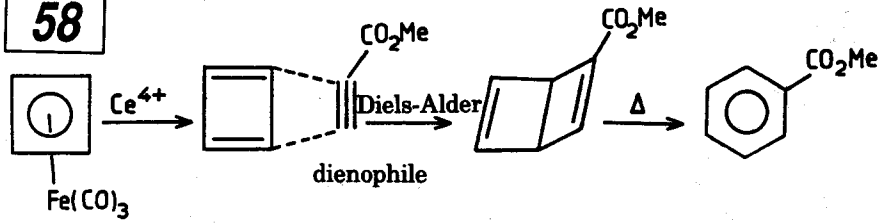
CYCLOBUTADIENE: DELOCALISED OR LOCALISED?

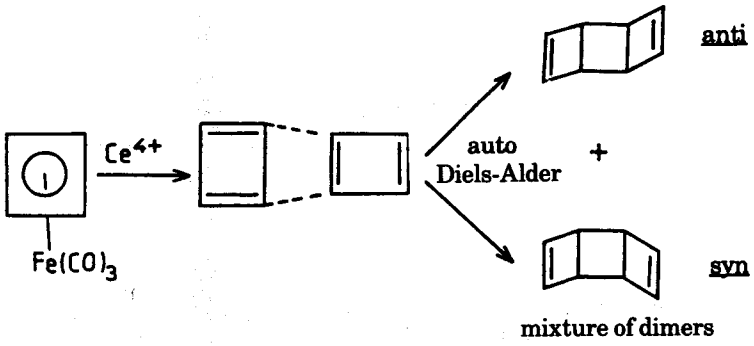
57



CYCLOBUTADIENES: METALLO COMPLEXES

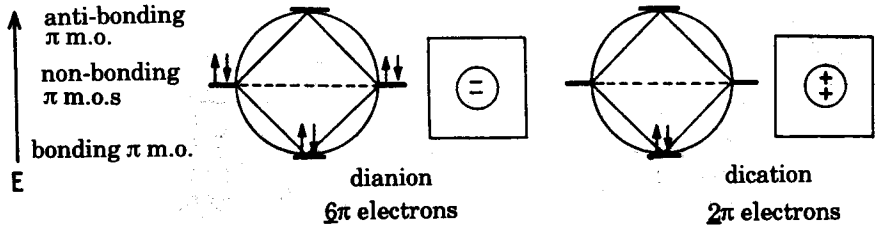
58





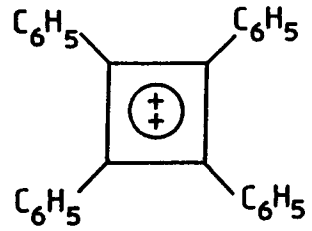
CYCLOBUTADIENE: NORMAL AND AUTO DIELS-ALDER REACTIONS

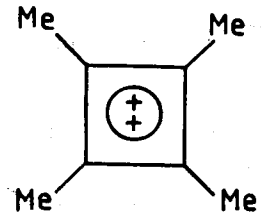
59



CYCLOBUTADIENYL DIANION AND DICATION

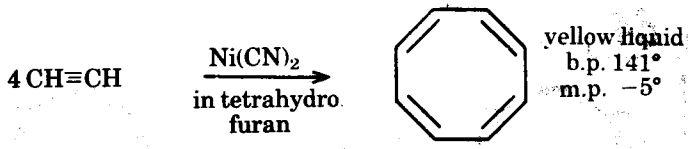
60





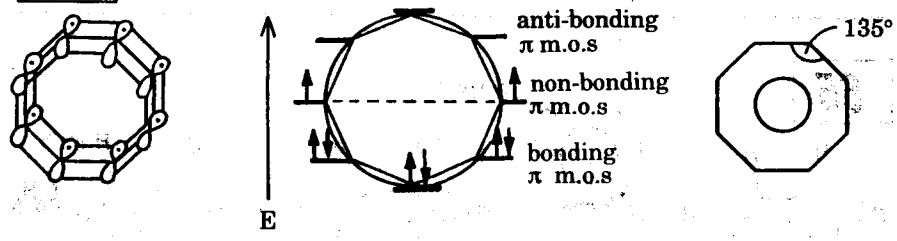
CYCLOBUTADIENYL DICATIONS

61



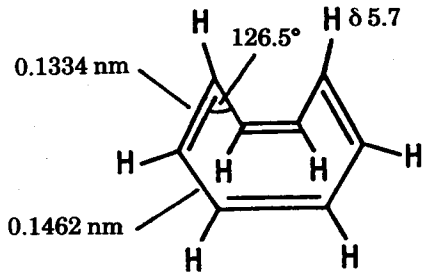
CYCLOOCTATETRAENE: PREPARATION

62



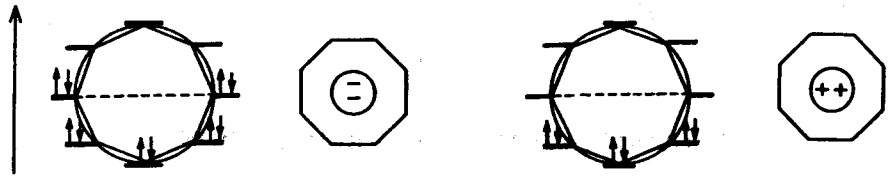
CYCLOOCTATETRAENE: F. AND M. POLYGON

63



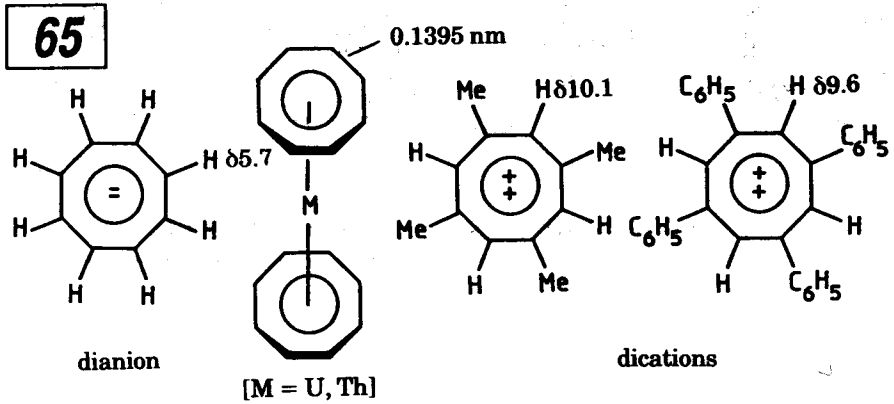
CYCLOOCTATETRAENE: SHAPE AND PHYSICAL DATA

64



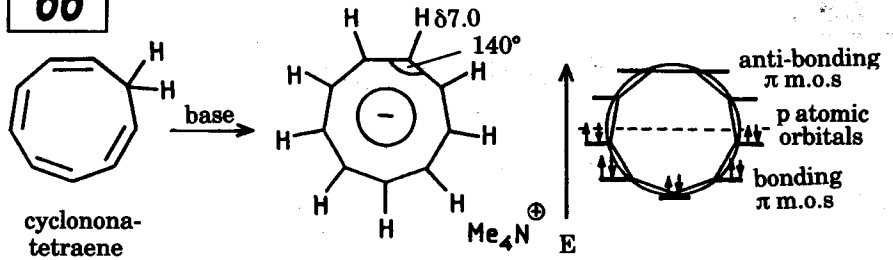
CYCLOTETRAENYL DIANION/DICATION: F. AND M. POLYGONS

65



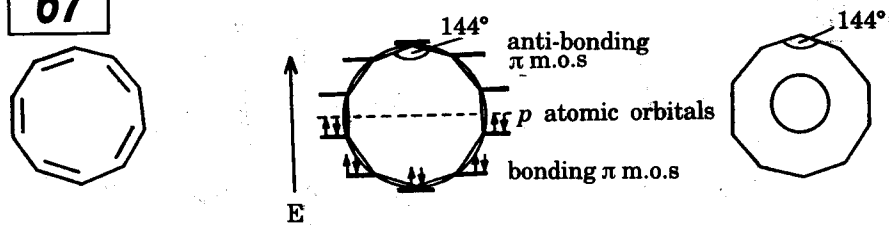
CYCLOOCTATETRAENYL DIANION AND DICATIONS

66



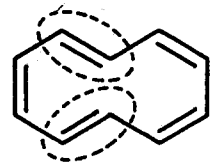
CYCLONONATETRAENYL ANION: F. AND M. POLYGON

67



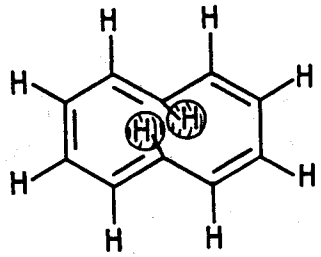
CYCLODECAPENTAENE: F. AND M. POLYGON

68



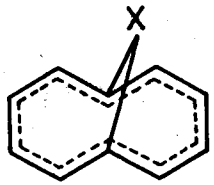
[10] ANNULENE

69

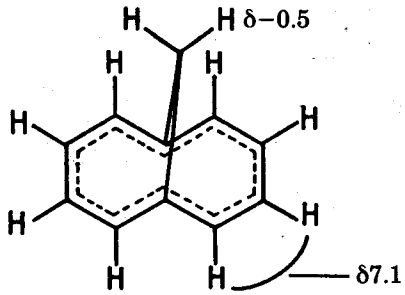


[10] ANNULENE: CROWDING OF THE TWO INTERNAL HYDROGENS

70

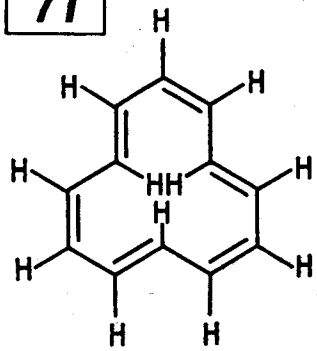


[X = CH_2, O, NH, NCOMe]



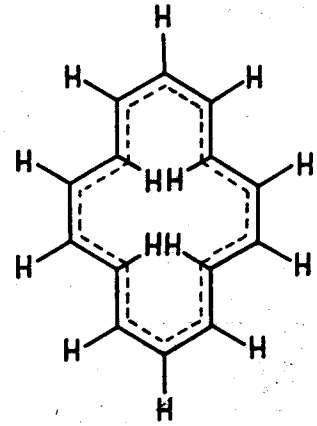
BRIDGED [10] ANNULENES: δ VALUES OF CH_2 COMPOUND

71



[12] annulene

(4*n*)

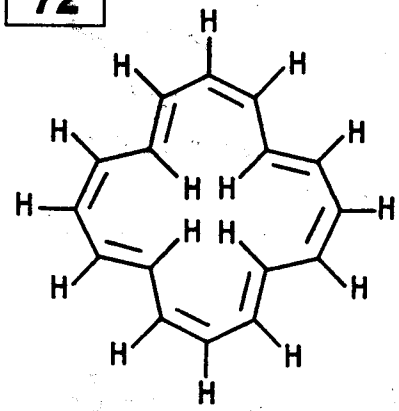


[14] annulene

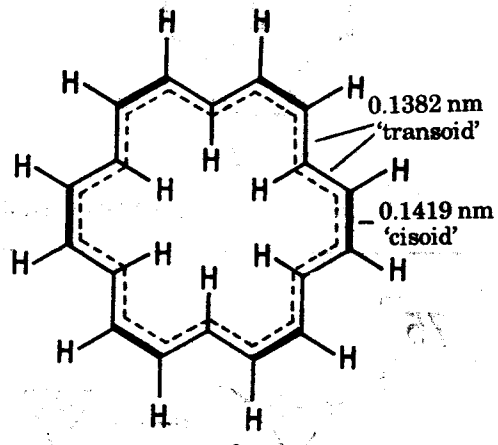
(4*n* + 2)

[12] AND [14] ANNULENES

72



(4*n*)

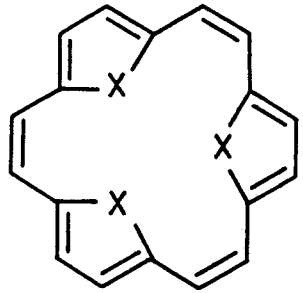


[18] annulene

(4*n* + 2)

[16] AND [18] ANNULENES

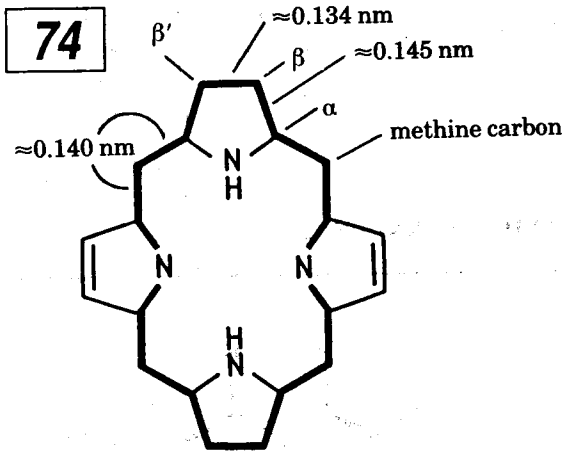
73



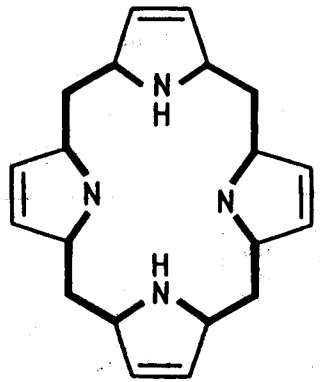
[X = O, S]

[18] ANNULENES: O AND S BRIDGED

74



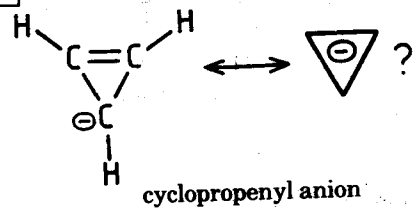
18 atom/18 πe ring



16 atom/18 πe ring

PORPHIN: DIMENSIONS

75



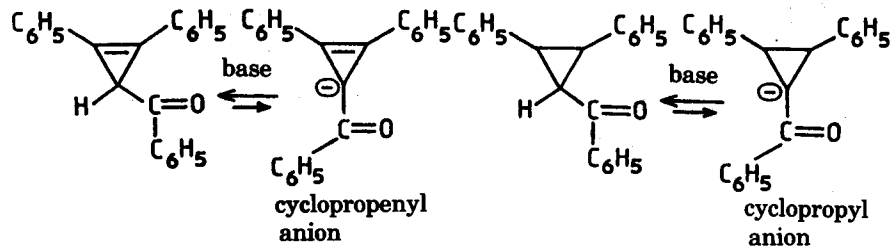
cyclopropenyl anion

$CH_2=CH-\overset{\ominus}{C}H_2$

allyl anion

CYCLOPROPENYL vs. ALLYL ANION : ANTI-AROMATIC?

76



cyclopropenyl anion

cyclopropyl anion

CYCLOPROPENYL vs. CYCLOPROPYL ANION : ANTI-AROMATIC?

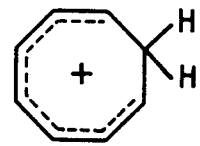
77

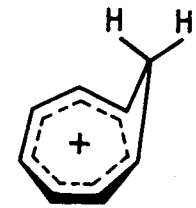
C_8H_8

$\xrightarrow[SbCl_5]{HCl}$ $C_8H_9^{\oplus}\ SbCl_6^{\ominus}$

CYCLOOCTATETRAENE : PROTONATION

78

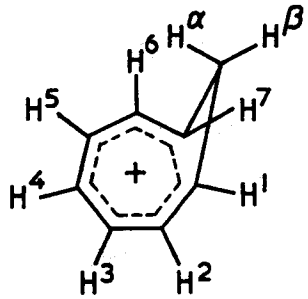




PROTONATED CYCLOOCTATETRAENE: ALTERNATIVE STRUCTURES

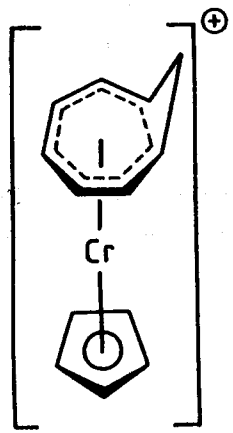
79

δ
8.5 ($H^2 - H^6$)
3.4 (H^1, H^7)
4.8 (H^8)
−0.6 (H^α)



PROTONATED CYCLOOCTATETRAENE: PROTON N.M.R DATA

80



HOMOTROPYLIUM CATION/CYCLOPENTADIENYL ANION Cr "SANDWICH"

FURTHER READING

GARRATT, P.J. *Aromaticity* (Wiley, 1986)

LEWIS, D and PETERS, D. *Facts and Theories of Aromaticity* (Macmillan, 1975)

LLOYD, D. *Non-benzenoid Conjugated Carbocyclic Compounds* (Elsevier, 1984)