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# AROMATICITY

Peter Sykes

ETGT CHEMISTRY CASSETTE

## CHEMISTRY CASSETTES

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Diagrams by Angela Saunders

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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.

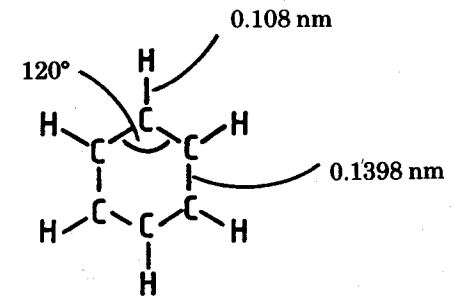
During the course of the programme you will, from time to time, be asked to **stop the tape** and answer questions — so have pencil and paper ready before you begin to listen. You will also be referred regularly to the reaction schemes in this workbook; each of these is numbered and you will be given 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

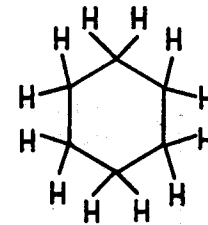
1



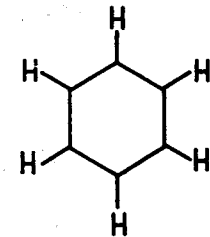
**BENZENE: SHAPE AND DIMENSIONS**

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2



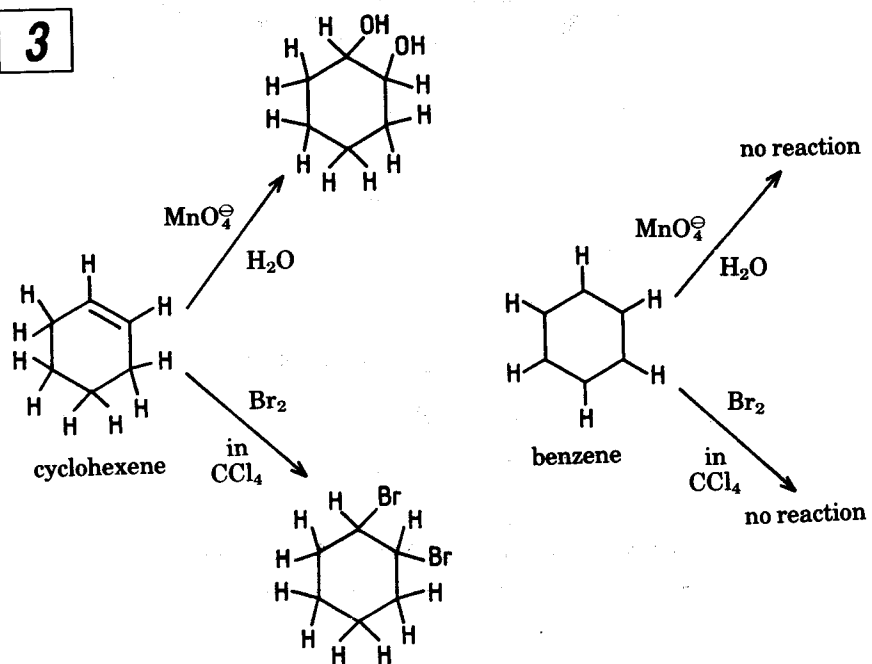
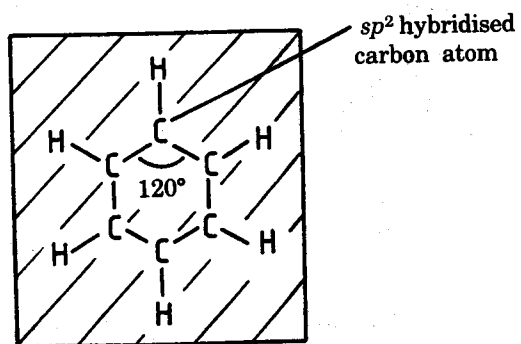
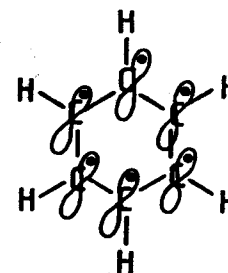
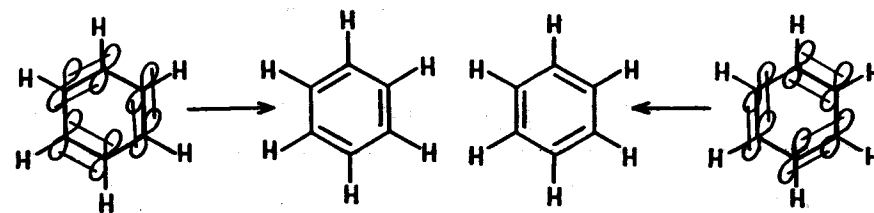
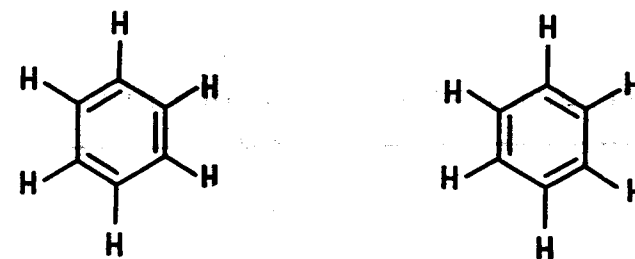
cyclohexane: C<sub>6</sub>H<sub>12</sub>  
saturated



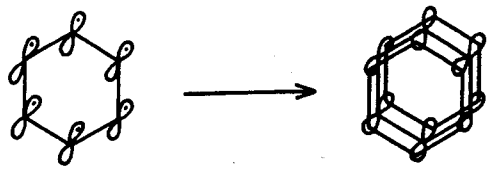
benzene: C<sub>6</sub>H<sub>6</sub>  
unsaturated

**CYCLOHEXANE/BENZENE COMPARISON**

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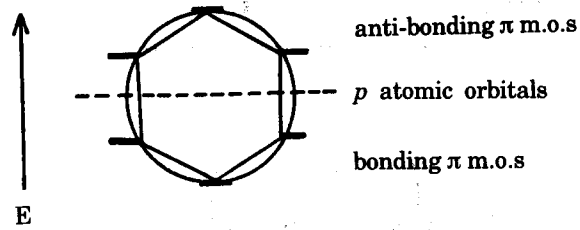
**3****4****TESTS FOR UNSATURATION****BENZENE: FLAT, REGULAR HEXAGON****5****BENZENE: SIX  $p$  ATOMIC ORBITALS****6****ADJACENT OVERLAP  $\rightarrow$  KEKULE STRUCTURES****7****KEKULE STRUCTURES: IRREGULAR HEXAGONS**

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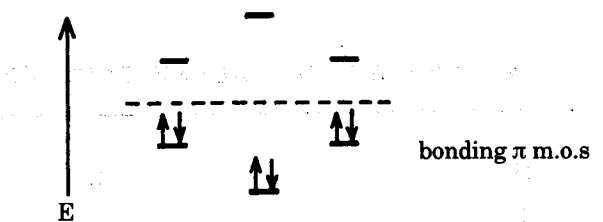
"ALL ROUND" OVERLAP OF *p* ORBITALS

9



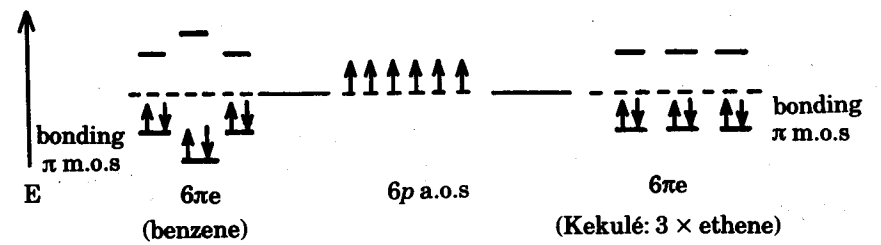
FROST AND MUSULIN POLYGON: BENZENE

10



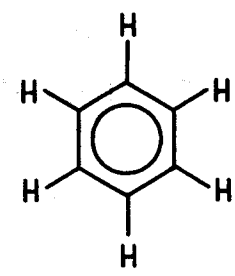
BENZENE: ELECTRON ALLOCATION TO M.O.s

11



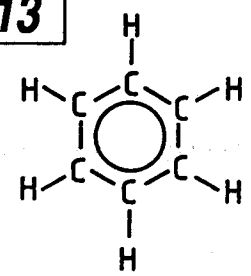
ELECTRON ALLOCATION: BENZENE vs. 3 x ETHENE

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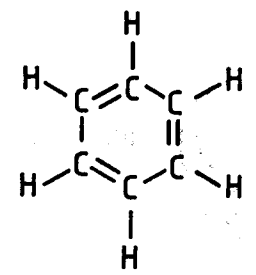


BENZENE: CURRENT REPRESENTATION

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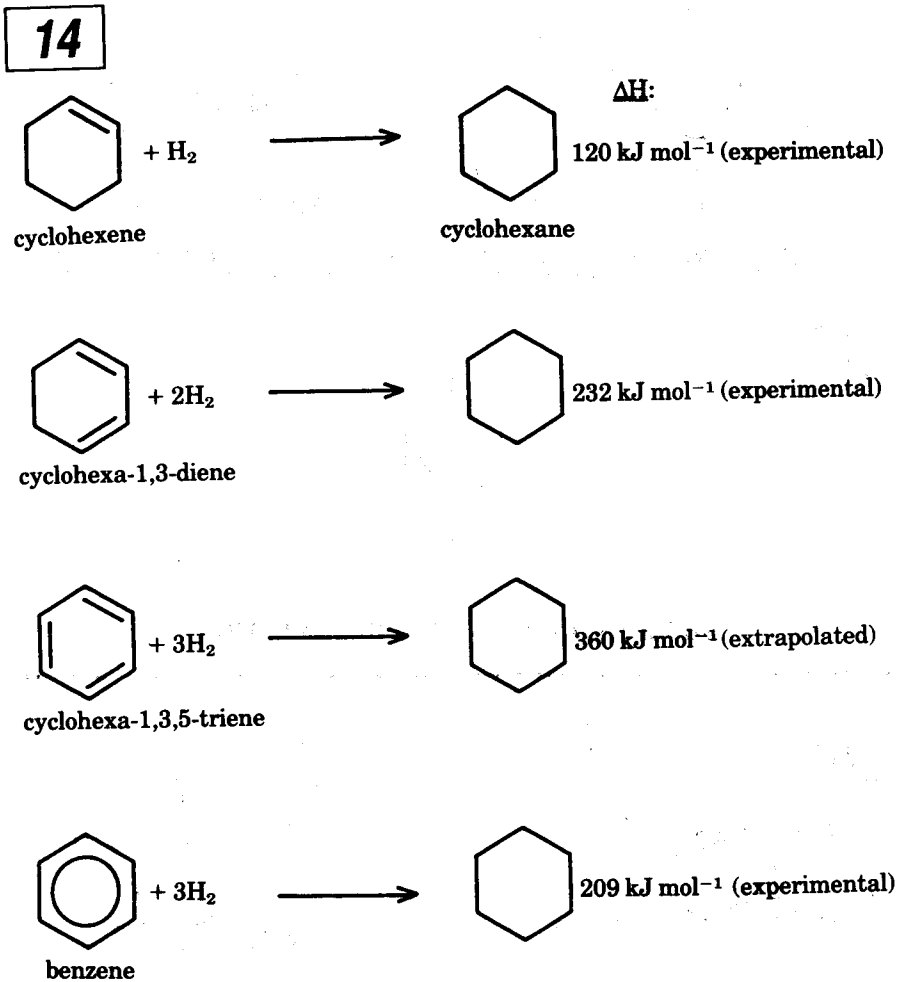


"real" benzene:  
3299 kJ mol<sup>-1</sup> (expt.)

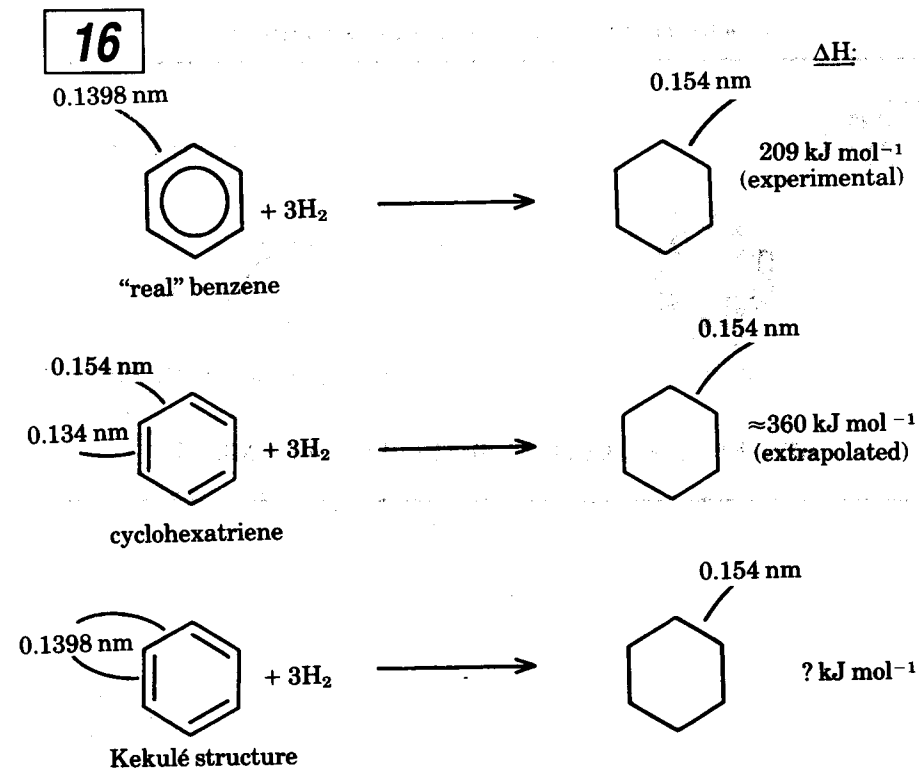
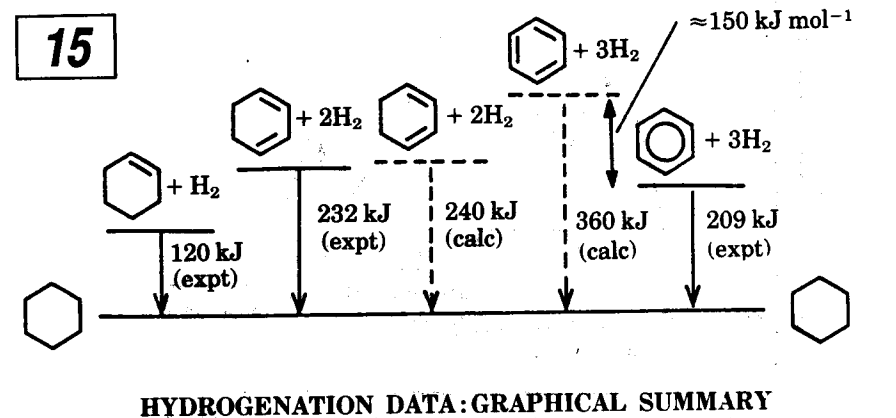


Kekulé structure:  
3449 kJ mol<sup>-1</sup> (calc.)

HEAT OF COMBUSTION DATA

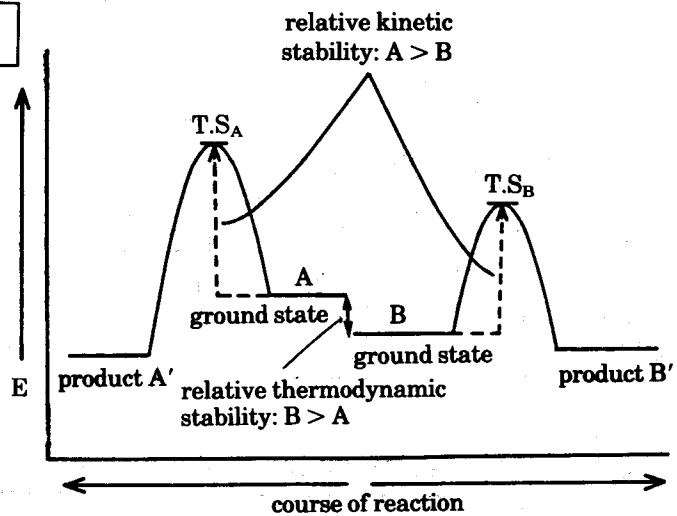


**HEAT OF HYDROGENATION DATA**



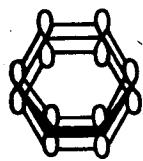
**VALIDITY OF HYDROGENATION DATA**

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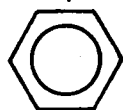


### THERMODYNAMIC vs. KINETIC STABILITY

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planarity

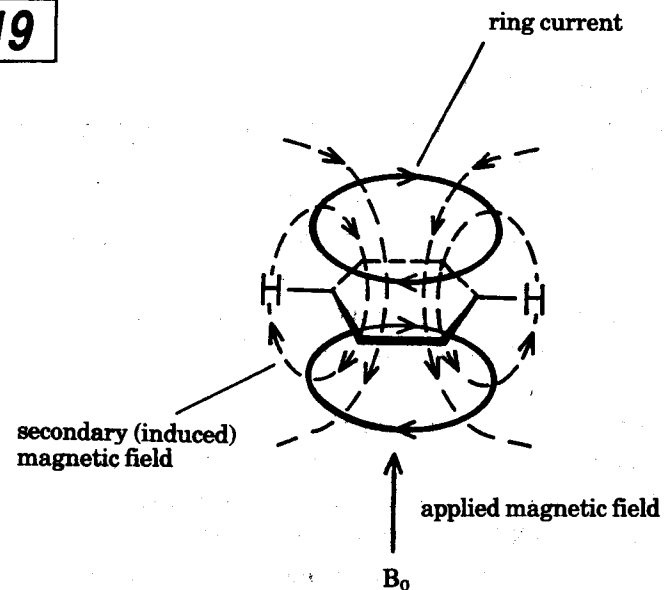


all C-C bond lengths the same

0.1398 nm

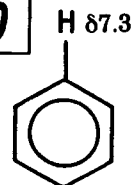
### BENZENE: "AROMATIC" SHAPE AND DIMENSIONS

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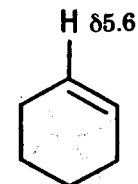


### N.M.R. SPECTROSCOPY: AROMATIC RING CURRENT

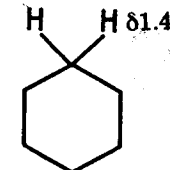
20



benzene



cyclohexene



cyclohexane

### COMPARISON OF PROTON CHEMICAL SHIFTS ( $\delta$ )

21

## 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

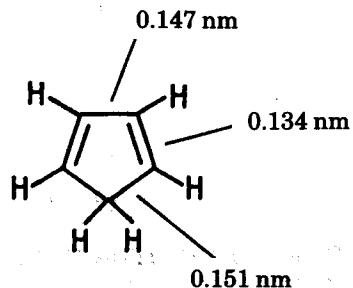
Data from X-ray diffraction, etc. Planarity, bond length values intermediate between C=C and C-C, and non-alternating. Gives basic information about whether molecule is "benzene-like".

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

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

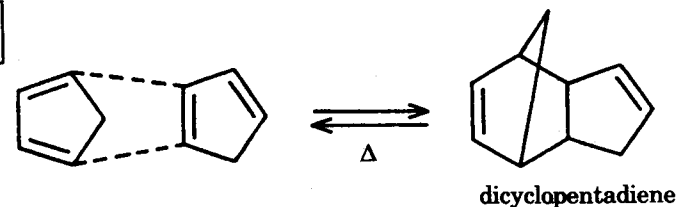
## CRITERIA FOR AROMATIC CHARACTER: SUMMARY

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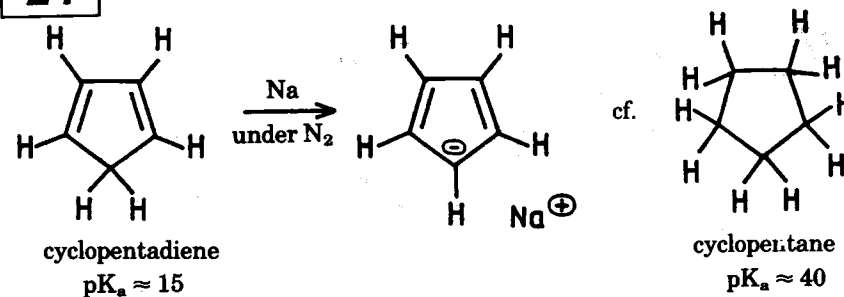
CYCLOPENTA-1,3-DIENE

23

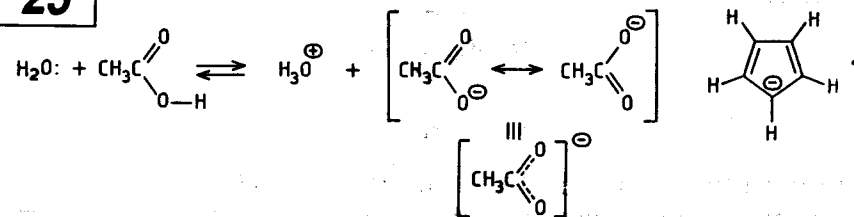


CYCLOPENTADIENE: DIMERISATION

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CYCLOPENTADIENE: ACIDITY ( $\text{pK}_a$ ) vs. CYCLOPENTANE

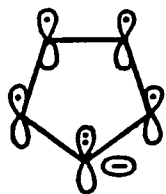
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ETHANOIC ACID: ACIDITY AND ANION STABILISATION

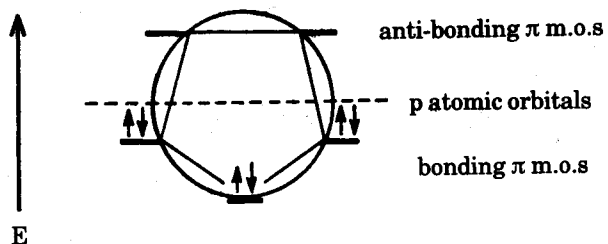


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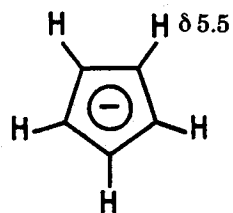
CYCLOPENTADIENYL ANION: *p* ORBITALS

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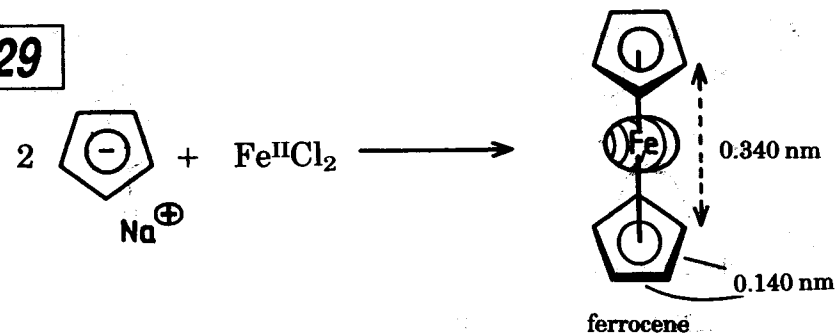
CYCLOPENTADIENYL ANION: FROST AND MUSULIN POLYGON

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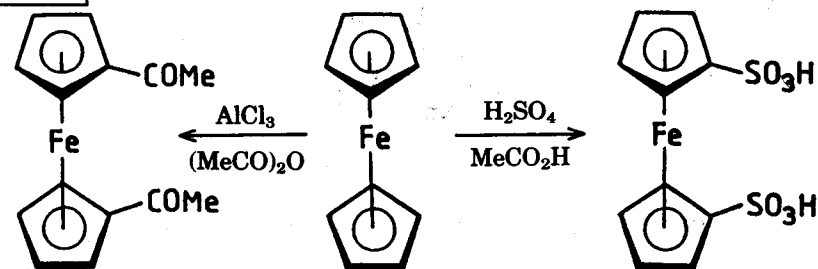
CYCLOPENTADIENYL ANION: REPRESENTATION AND  $\delta$  VALUE

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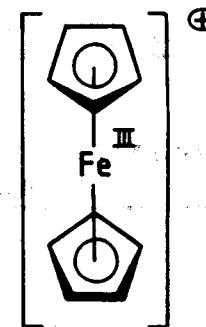
FERROCENE: PREPARATION AND DIMENSIONS

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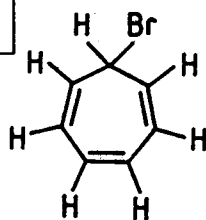
FERROCENE: F. C. ACYLATION AND SULPHONATION

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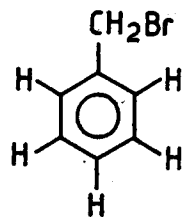


FERRICENIUM CATION

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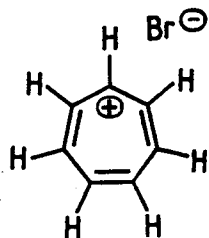
cycloheptatrienyl bromide



benzyl bromide

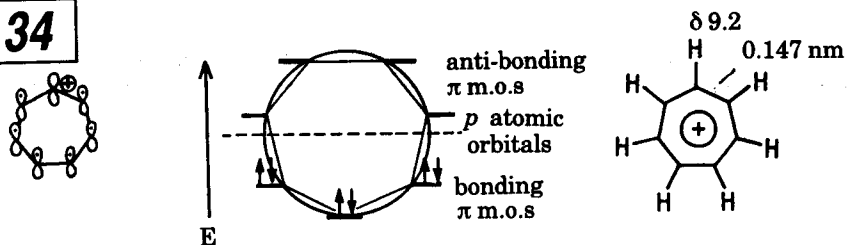
ISOMERIC CYCLOHEPTATRIENYL (TROPYLIUM) AND BENZYL BROMIDES

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CYCLOHEPTATRIENYL BROMIDE: ION PAIR

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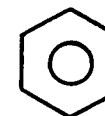


CYCLOHEPTATRIENYL CATION: FROST AND MUSULIN POLYGON AND DIMENSIONS

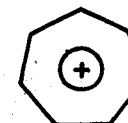
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cyclopentadienyl anion



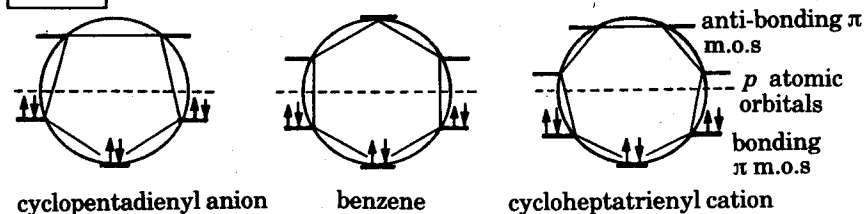
benzene



cycloheptatrienyl cation

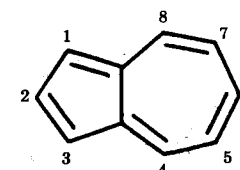
COMPARISON OF STRUCTURAL REPRESENTATIONS

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

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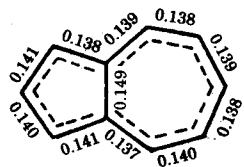


AZULENE

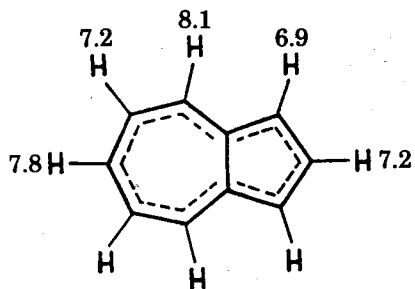
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AZULENE: *p* ORBITAL OVERLAP

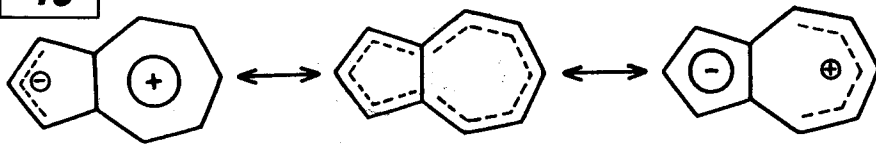
39



bond lengths (nm)

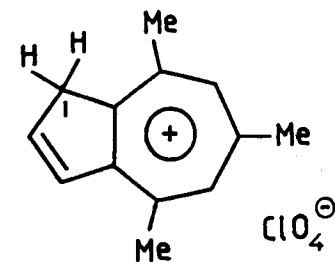
 $\delta$  valuesAZULENE: DIMENSIONS AND  $\delta$  VALUES

40



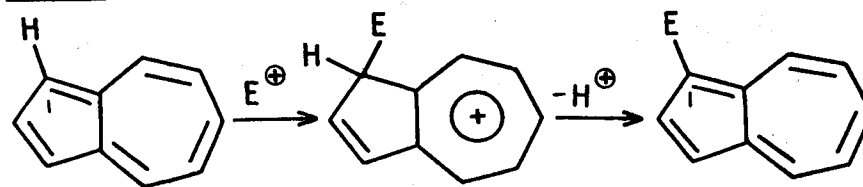
AZULENE: DIPOLAR CHARACTER?

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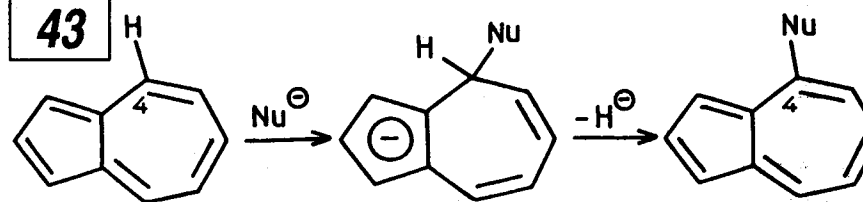
AZULENE: PROTONATION OF A DERIVATIVE

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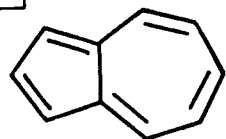
AZULENE: ELECTROPHILIC SUBSTITUTION

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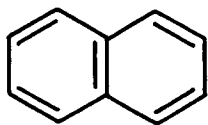
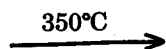


AZULENE: NUCLEOPHILIC SUBSTITUTION

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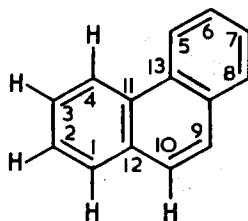
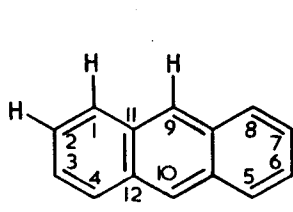
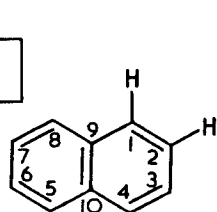
azulene



naphthalene

AZULENE: ISOMERISATION TO NAPHTHALENE

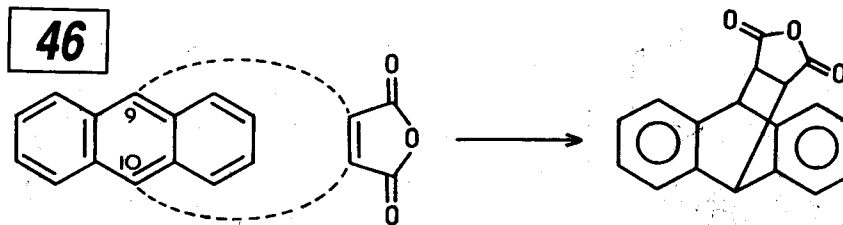
45



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

NAPHTHALENE, ANTHRACENE, PHENANTHRENE: PHYSICAL DATA

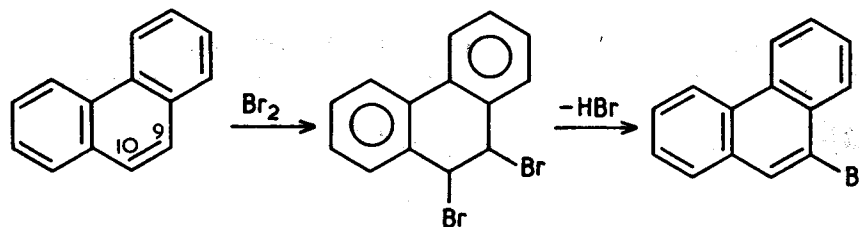
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anthracene

maleic anhydride

Diels-Alder adduct



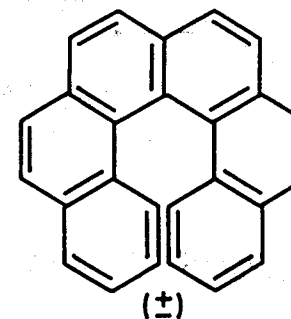
phenanthrene

9,10-dibromide

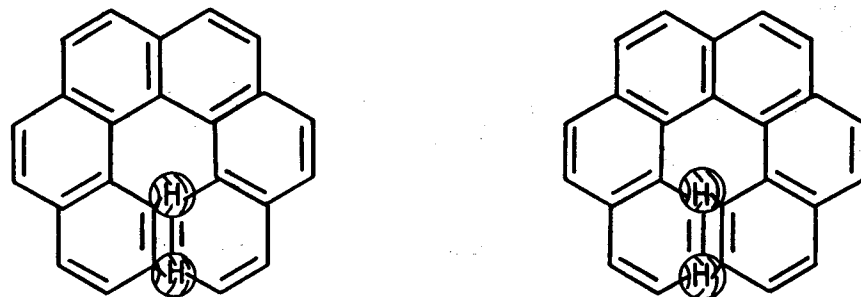
9-bromo

ANTHRACENE, PHENANTHRENE: DOUBLE BOND CHARACTER

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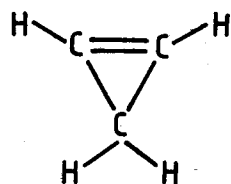
26  $\pi$  ELECTRON HEXACYCLIC SYSTEM: CHIRAL

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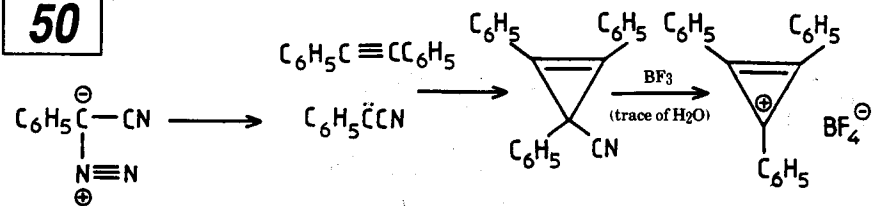
HEXAHELICENE: STRUCTURE OF MIRROR IMAGES

49



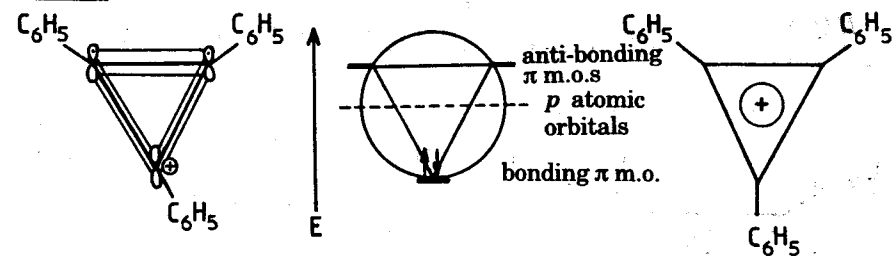
CYCLOPROPENE

50



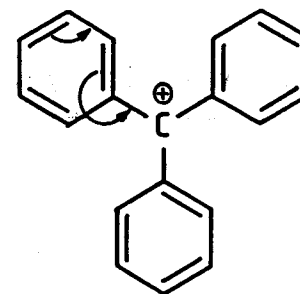
SUBSTITUTED CYCLOPROPENE AND CYCLOPROPENYL CATION: PREPARATION

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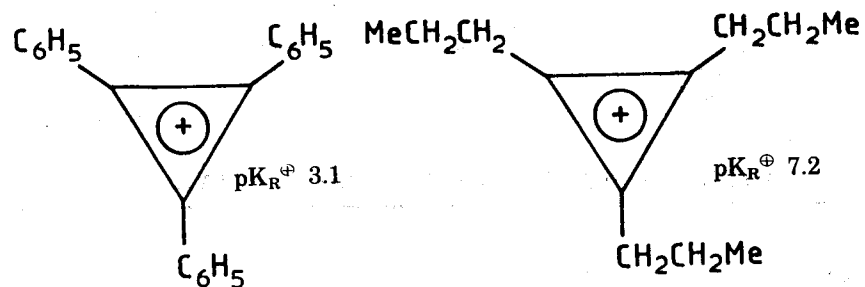
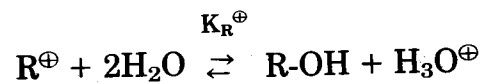
CYCLOPROPENYL CATION: F. AND M. POLYGON

52

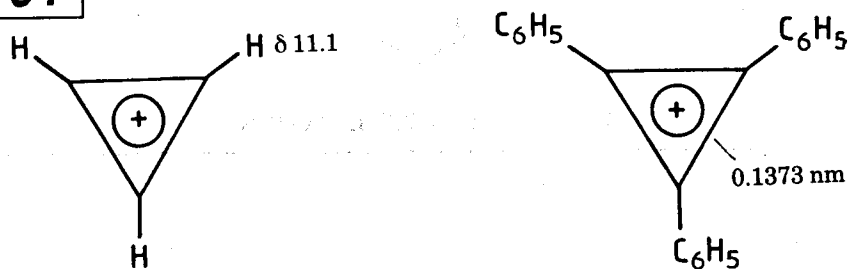


TRIPHENYLMETHYL CATION

53

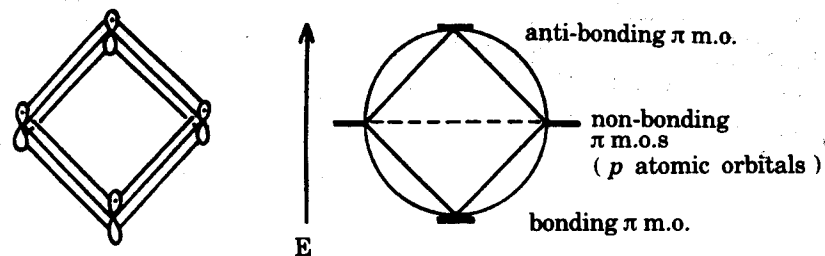
CYCLOPROPENYL CATIONS:  $pK_R^{\oplus}$  VALUES

54



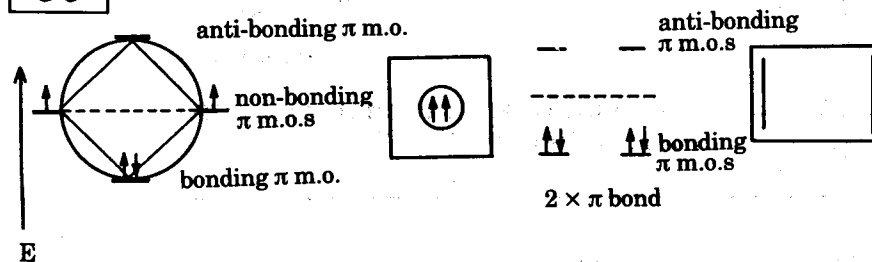
CYCLOPROPENYL CATIONS: PHYSICAL DATA

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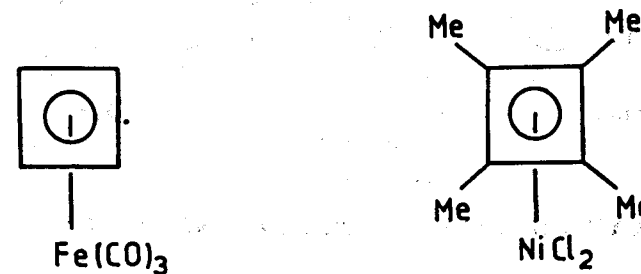
CYCLOBUTADIENE: F. AND M. POLYGON

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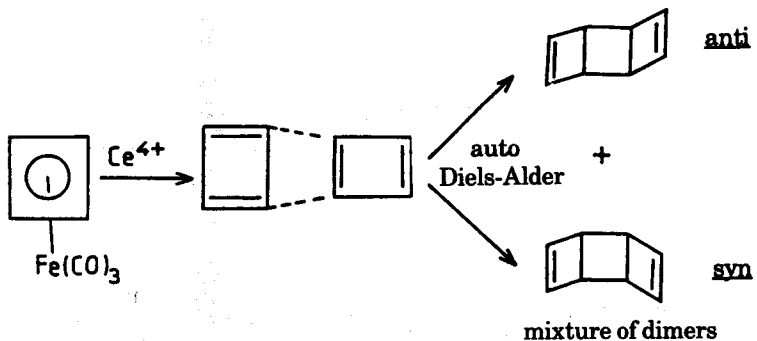
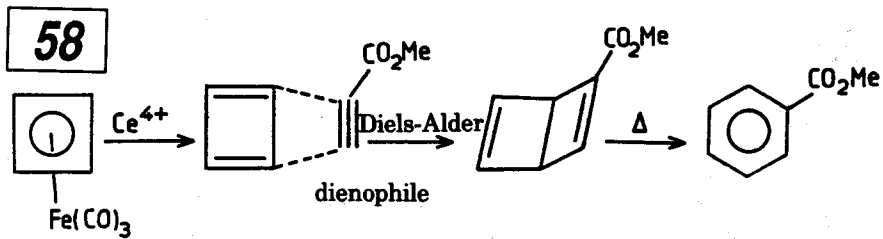


CYCLOBUTADIENE: DELOCALISED OR LOCALISED?

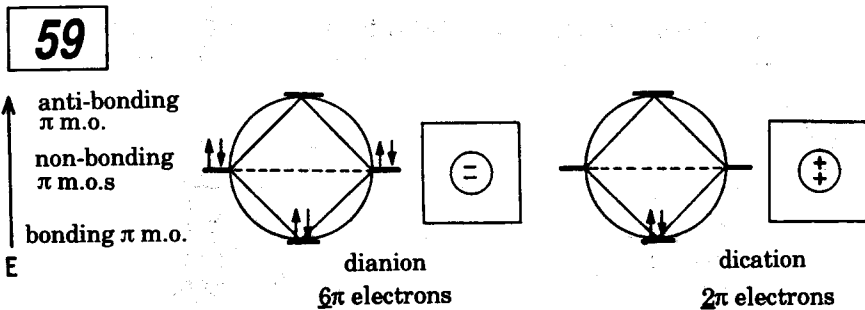
57



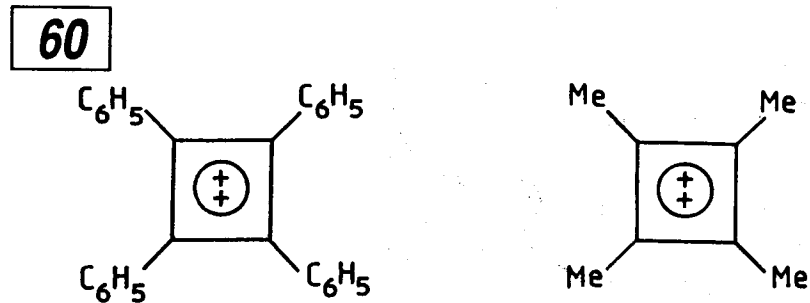
CYCLOBUTADIENES: METALLO COMPLEXES



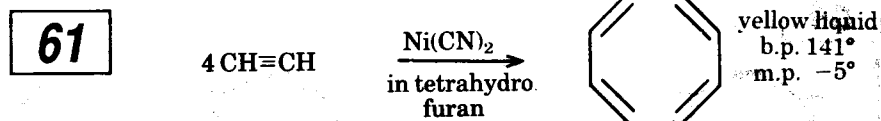
**CYCLOBUTADIENE: NORMAL AND AUTO  
DIELS-ALDER REACTIONS**



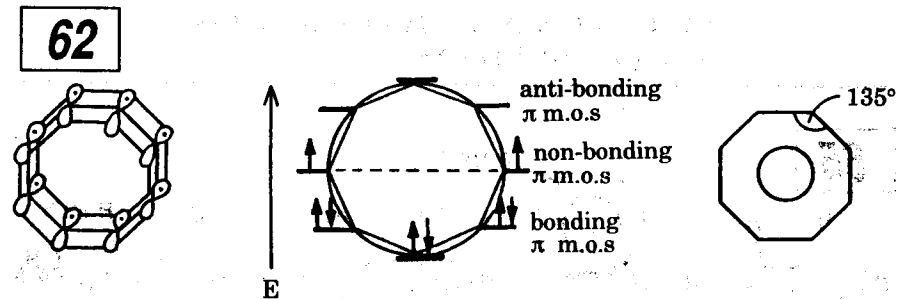
**CYCLOBUTADIENYL DIANION AND DICATION**



**CYCLOBUTADIENYL DICATIONS**

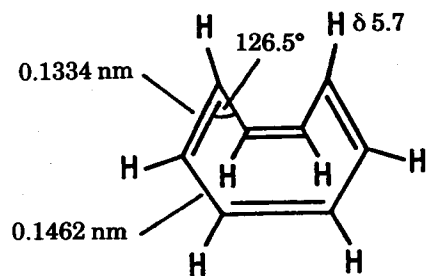


**CYCLOOCTATETRAENE: PREPARATION**



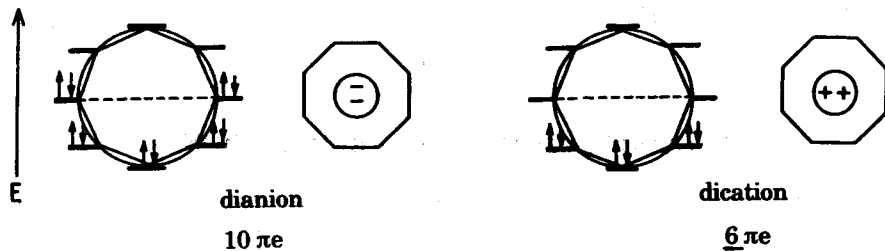
**CYCLOOCTATETRAENE: F. AND M. POLYGON**

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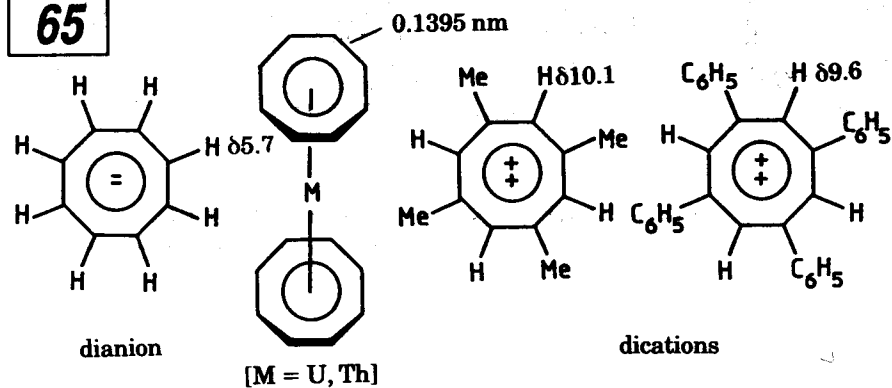


## CYCLOOCTATETRAENE: SHAPE AND PHYSICAL DATA

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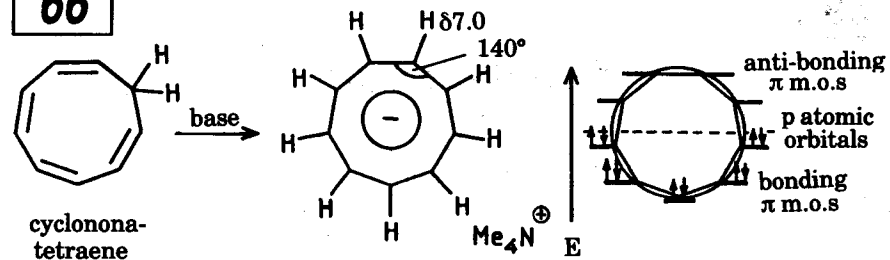
CYCLOOCTATETRAENYL DIANION/DICATION:  
F. AND M. POLYGONS

65



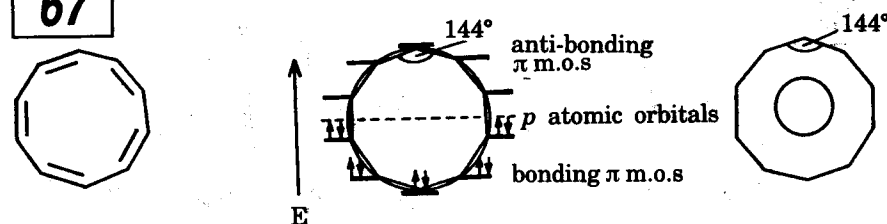
## CYCLOOCTATETRAENYL DIANION AND DICATIONS

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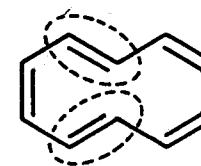
## CYCLONONATETRAENYL ANION: F. AND M. POLYGON

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## CYCLODECAPENTAENE: F. AND M. POLYGON

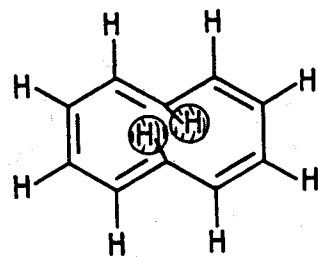
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## [10] ANNULENE

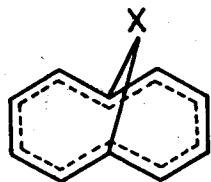
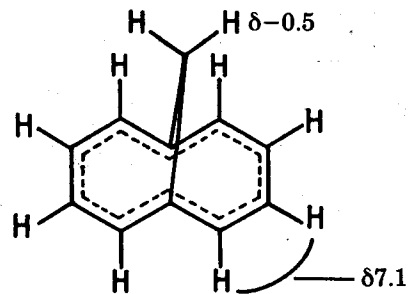


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[10] ANNULENE: CROWDING OF THE TWO INTERNAL HYDROGENS

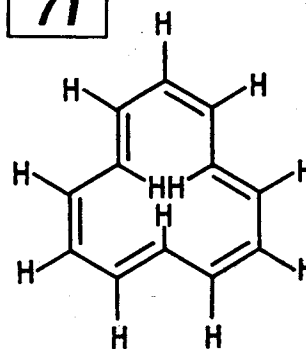
70

[X = CH<sub>2</sub>, O, NH, NCOMe]

87.1

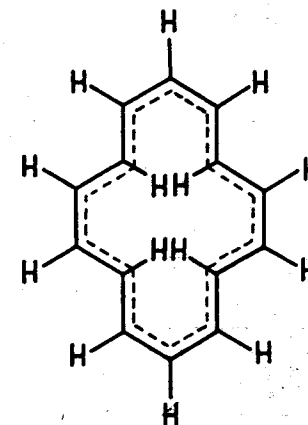
BRIDGED [10] ANNULENES:  $\delta$  VALUES OF CH<sub>2</sub> COMPOUND

71



[12] annulene

(4n)

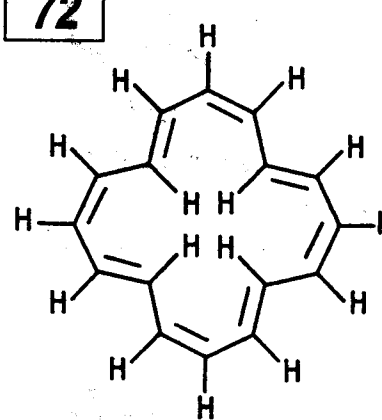


[14] annulene

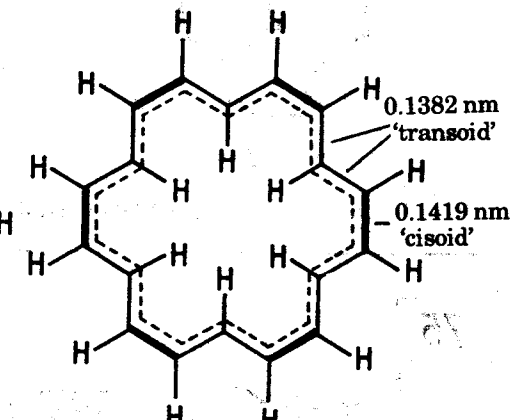
(4n + 2)

[12] AND [14] ANNULENES

72



(4n)

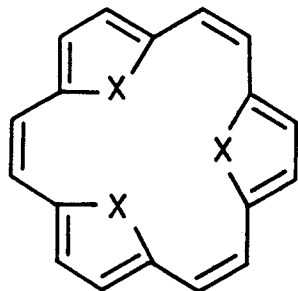


[18] annulene

(4n + 2)

[16] AND [18] ANNULENES

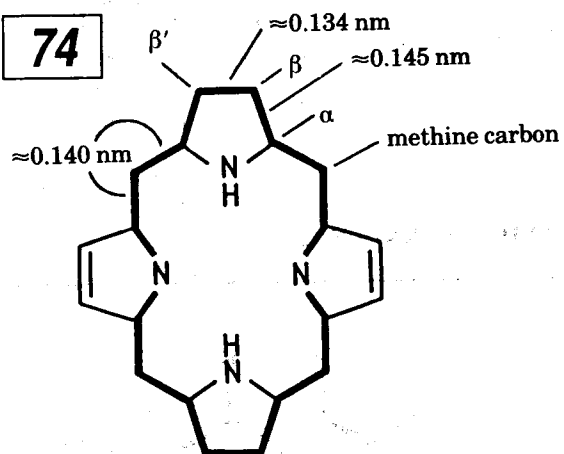
73



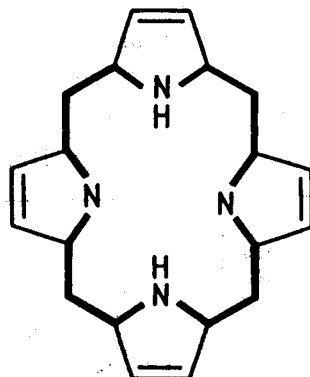
[X = O, S]

[18] ANNULENES: O AND S BRIDGED

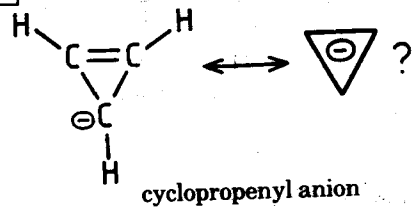
74

18 atom/18  $\pi$ e ring

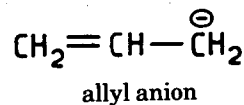
PORPHIN: DIMENSIONS

16 atom/18  $\pi$ e ring

75

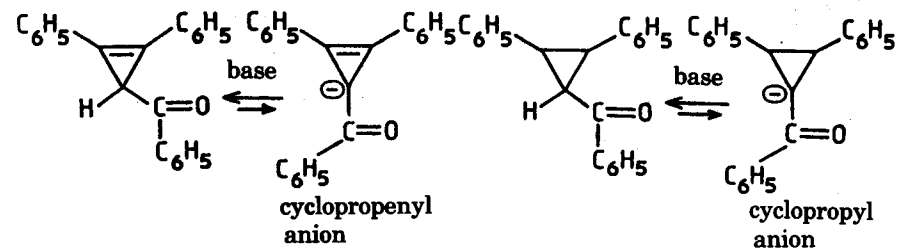


cyclopropenyl anion



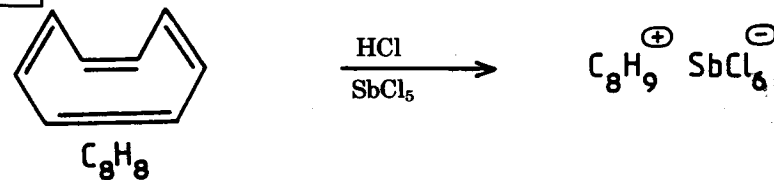
CYCLOPROPENYL vs. ALLYL ANION : ANTI-AROMATIC?

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CYCLOPROPENYL vs. CYCLOPROPYL ANION : ANTI-AROMATIC?

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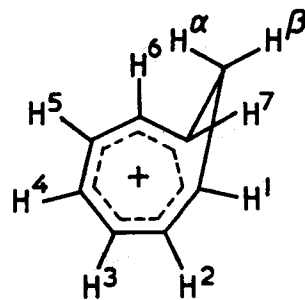
CYCLOOCTATETRAENE : PROTONATION

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PROTONATED CYCLOOCTATETRAENE:  
ALTERNATIVE STRUCTURES

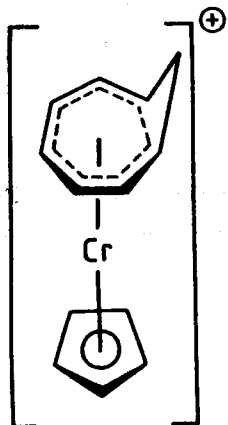
79

$\delta$   
 8.5 (H<sup>2</sup> - H<sup>6</sup>)  
 3.4 (H<sup>1</sup>, H<sup>7</sup>)  
 4.8 (H<sup>6</sup>)  
 -0.6 (H <sup>$\alpha$</sup> )



**PROTONATED CYCLOOCTATETRAENE:  
 PROTON N.M.R DATA**

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**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)