To Bjorn Bartels, PhD
Scientist and Human
Who will be missed

Aromaticity

Ramil Baiazitov

October 29, 2002

Outline

1. **History of aromaticity and different kinds of it**
2. **Criteria of aromaticity and antiaromaticity**
   - Energetic criteria
   - Structural criteria
   - Chemical criteria
   - Magnetic criteria (ring current)
     - NMR chemical shift
     - Magnetic susceptibility exaltation and anisotropy
3. **Kinds of aromaticity** (anti-,homo-, schizo-).

What was aromaticity?

<1825 – distinctive "aromatic" smell

<1865 – hign C:H ratio, still stable

1865 – benzene structure (Kekule)

1866 – substitution is more favorable than addition (Erlenmeyer)

1910 – exalted diamagnetic susceptibility (Pascal)

1925 – electron sextet and heteroaromaticity (Armit-Robinson)

1931 – theory of cyclic (4n+2) π systems (Huckel)

1936 – ring current theory (Pauling)

1937 – London diamagnetism

1956 – ring current effects on NMR shifts (Pople)

P. Schleyer and H. Jiao, *Pure and Appl. Chem.*, **1996**, *68*, 209

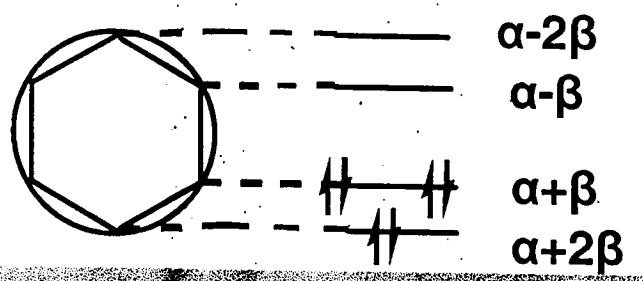
Summary of the definitions

1. **Chemical behavior – reversion to type**
2. **Structural –bond length equalization due to delocalization**
3. **Energetic – enhanced stability**
4. **Magnetic – ring current effects**
   - anomalous chemical shifts
   - large magnetic anisotropies
   - diamagnetic susceptibility exaltation

P. Schleyer and H. Jiao, *Pure and Appl. Chem.*, **1996**, *68*, 209

Huckel rule

$E_J=\alpha+2\beta\cos(2\pi J/N)$



$E_{loc}= 6(\alpha+\beta)$ or

$3(\alpha+2.0699\beta)+3(\alpha+0.4660\beta)=$

$6\alpha+7.61\beta$

$E_\pi=6\alpha+8\beta \quad \Delta E=E_\pi-E_{loc}=+0.39\beta$

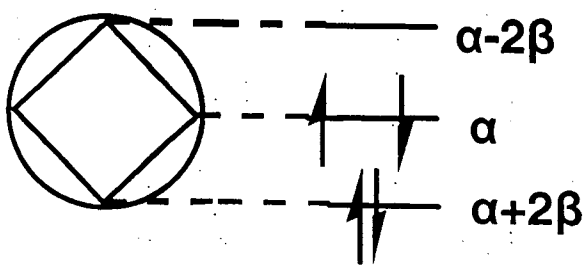


Table I. Calculated Hückel π-Bond Energies of Carbon–Carbon Double Bonds and Carbon–Carbon Single Bonds of Acyclic Polyenes

Designation[a]	Type of bond	Calculated π-bond energy, β
23	$H_2C{=}CH$	2.0000[b]
22	$HC{=}CH$	2.0699
22′	$H_2C{=}C$	2.0000[b]
21	$HC{=}C$	2.1083
20	$C{=}C$	2.1716
12	$HC{-}CH$	0.4660
11	$HC{-}C$	0.4362
10	$C{-}C$	0.4358

[a] The first index gives the bond order, the second the number of attached hydrogens. [b] Arbitrarily assigned.

$E_{loc}=2(\alpha+2.0699\beta)+2(\alpha+0.4660\beta)=$

$4\alpha+5.07\beta$

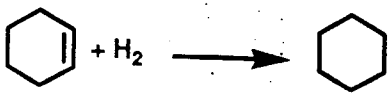
$E_\pi=4\alpha+4\beta \quad \Delta E=E_\pi-E_{loc}=-1.07\beta$

B.A. Hess, Jr., and L. J. Schaad, *JACS*, **1971**, *93*, 305

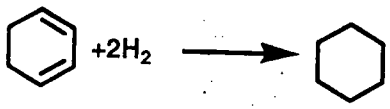
Criteria of aromaticity. Energetic criteria

RE=ΔH^{o}_{a}(PhH)-6E(C-H)-3E(C-C)-3E(C=C)

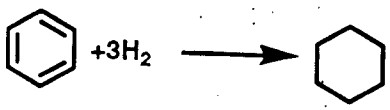
Hydrogenation:



ΔH=-28.3kcal/mol

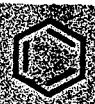


ΔH=-54.8 kcal/mol(-28.3x2+1.8)



ΔH=-49.1kcal/mol(-28.3x3+35.8)

ΔH=35.8kcal/mol=
5.97kcal/π-electron=RE

Isodesmic :  +6CH4->3C2H6+3C2H4 ΔH=64.2kcal/mol

Homodesmotic :  +3C2H4->3*trans*-butadiene ΔH=21.6kcal/mol

Hyper-Homodesmotic :  +3CH2=CH-CH=CH2 -> 3CH2=CH-CH=CH-CH=CH2 ΔH=23.4kcal/mol(calc)

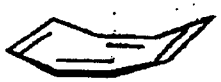
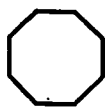
From V.I.Minkin et.al. *Aromaticity and Antiaromaticity….*,Wiley: New York; **1994**

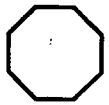
Criteria of aromaticity. Energetic criteria


+4CH4—>2CH2=CH2+2CH3—CH3 ΔH=-70kcal/mol


+4CH4—>1CH2=CH2+3CH3—CH3 ΔH=-28kcal/mol – strain energy

$\Delta\Delta H$=52kcal/mol – aromatic destabilization energy


+4H2->  ΔH=-100kcal/mol


+H2->  ΔH=-23kcal/mol =>$\Delta\Delta H$=4x23-100=8kcal/mol

4CH3F=3CH4+CF4 ΔH=-35.8kcal/mol

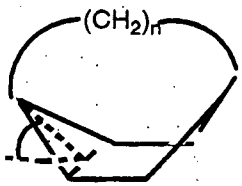
Criteria of aromaticity. Structural criteria.

π-delocalization=>planar geometry+bond length equalization,cyclic

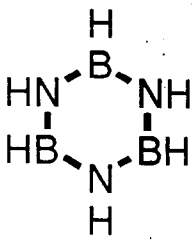
1.397A

1.565A vs. 1.344/1.355A

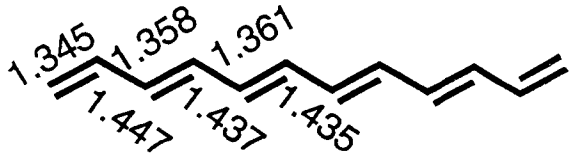
[*n*]-*para*-cyclophanes

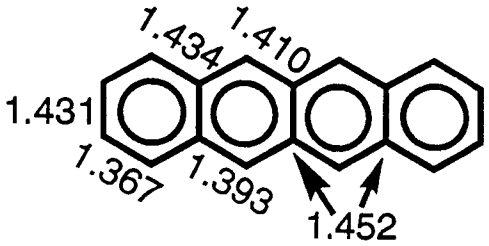


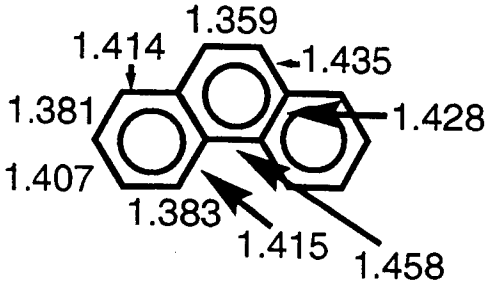
n=5 φ=23.7
n=6 φ=18.6
n=7 φ=14.2
n=8 φ=8.4



bond alteration 0.025A

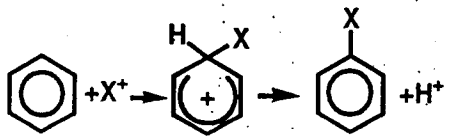


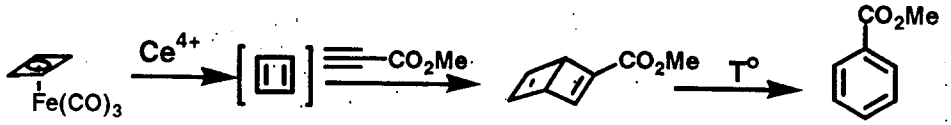


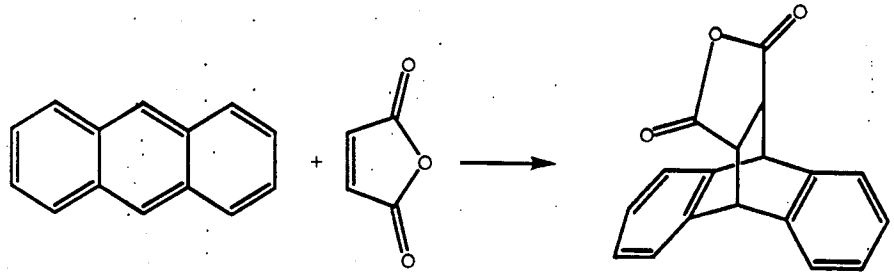


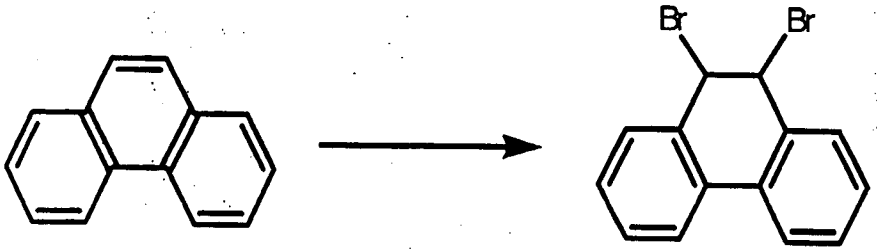
P. Schleyer and H. Jiao, *Pure and Appl. Chem.*, **1996**, *68*, 209
From V.I.Minkin et.al. *Aromaticity and Antiaromaticity….*,Wiley: New York; **1994**

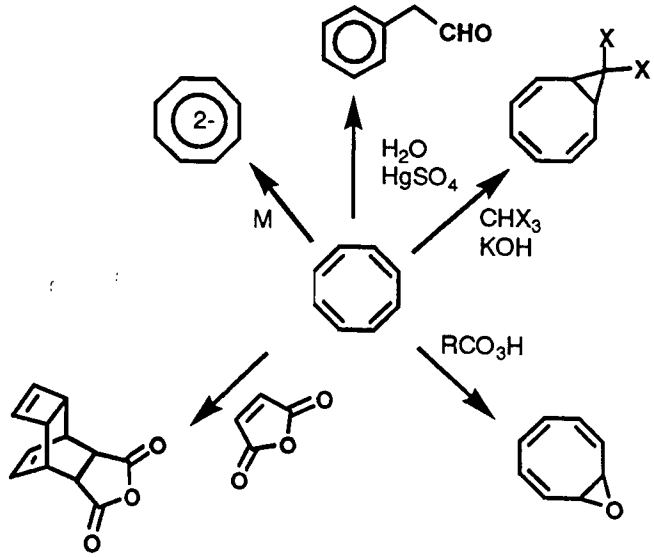
Criteria of aromaticity. Chemical criteria.











Criteria of aromaticity. Magnetic criteria.

A. Magnetic Susceptibility Exaltation and Anisotropy

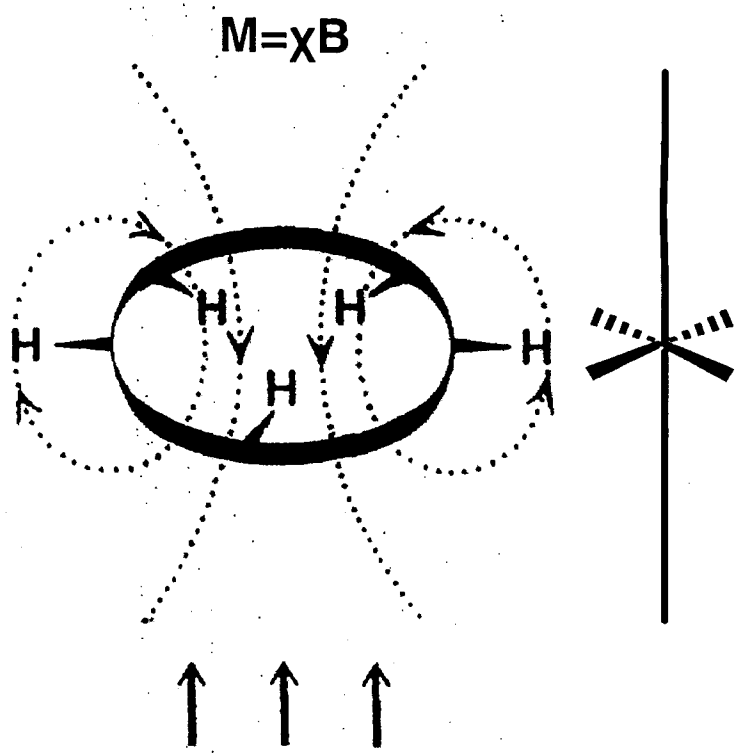


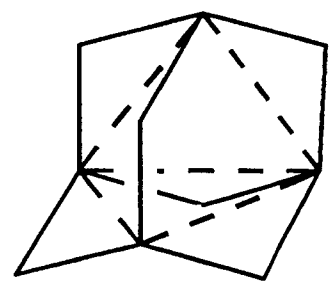
Fig. 1.—Diagram of magnetic field associated with a ring current in a monocyclic system.

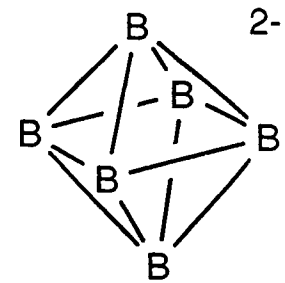
$\Delta\chi = \chi_{zz} - 1/2(\chi_{xx} + \chi_{yy})$-anisotropy of magnetic susceptibility

$\underline{\chi} = 1/3(\chi_{xx} + \chi_{yy} + \chi_{zz})$– mean molar magnetic susceptibility (isotropic media)

$\Lambda = \underline{\chi} - (\Sigma\chi A + n\lambda C = C) = \underline{\chi} - \chi_{calc}$

2+





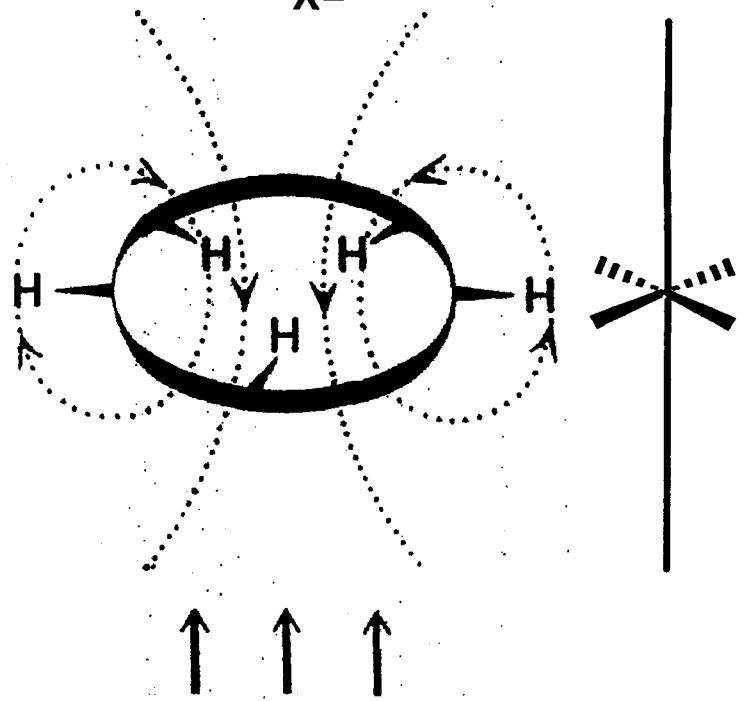
χanis	**0.0**	**0.0**
Λ	**-51.1**	**-49.6**

P. Schleyer and H. Jiao, *Pure and Appl. Chem.*, **1996**, *68*, 209

Criteria of aromaticity. Magnetic criteria.

A. Magnetic Susceptibility Exaltation and Anisotropy

$M=\chi B$



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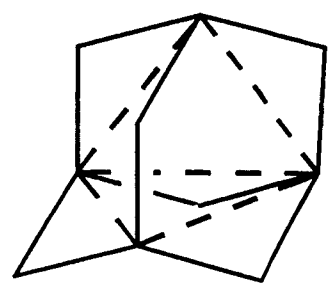
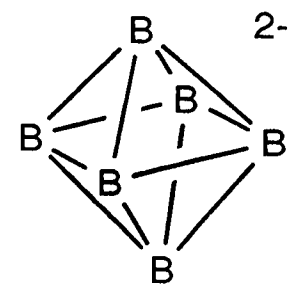
2+





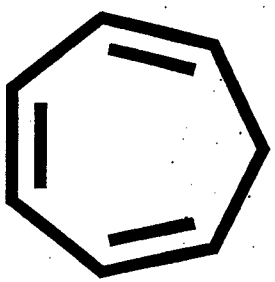
χanis	0.0	0.0
Λ	-51.1	-49.6

P. Schleyer and H. Jiao, *Pure and Appl. Chem.*, **1996**, *68*, 209

Criteria of aromaticity. Magnetic criteria.

A. Magnetic Susceptibility Exaltation and Anisotropy

	χ		χ		Λ		χ_{exp}/χ_{calc}
CH2	11.36	S	16.9	C=C	+5.5	hexane	74.3/73.1
H	2	N	9	CH3	-.85	methanol	21.9/22.0
C	7.36	Cl	18.5	C=C-C=C	+10.6	MeCN	27.6/26.9
O(alc)	5.3	Br	27.8	C≡C	+0.8	EtI	68.2/68.0
O(ald/ket)	6.4	I	42.2	N=N	+0.8	MEK	46.1/51.3
CO2(acids)	15.15						



6C2*-H =6(3.2)=19.2
2C2-H =2(3.8)=7.6
2C-C* =2(2.6)=5.2
5C*-C* =5(2.4)=12.0
3C=C =3(2.2)=6.6
7xinner e-core=7(0.15)=1.05

Xcalc =51.65
Λ 59.8-51.65=8.1

Calculated anisotropies

Aromatics	χ_{anis}	Λ
benzene	-62.9	-13.4
$C_5H_5^-$	-67.7	-17.2
napthalene	-130.3	-28.2
pyrrole	-48.1	-12.1
azulene	-144	-42.9
C_4H_4	28.7	18
$C_5H_5^+$	58.1	32.6
C_8H_8	146.3	60.4
pentalene	12.8	30.9
heptalene	168.3	76.7

P. Schleyer and H. Jiao, *Pure and Appl. Chem.*, **1996**, *68*, 209
Hyp J. Dauben, Jr., James D. Wilson, and John L. Laity *JACS*, **1968**, *90*, 811
Dr.W.Haberditzl, *Angew.Chem.Int.Ed.Eng.*,**1966**, *3*, 288

Criteria of aromaticity. Magnetic criteria.

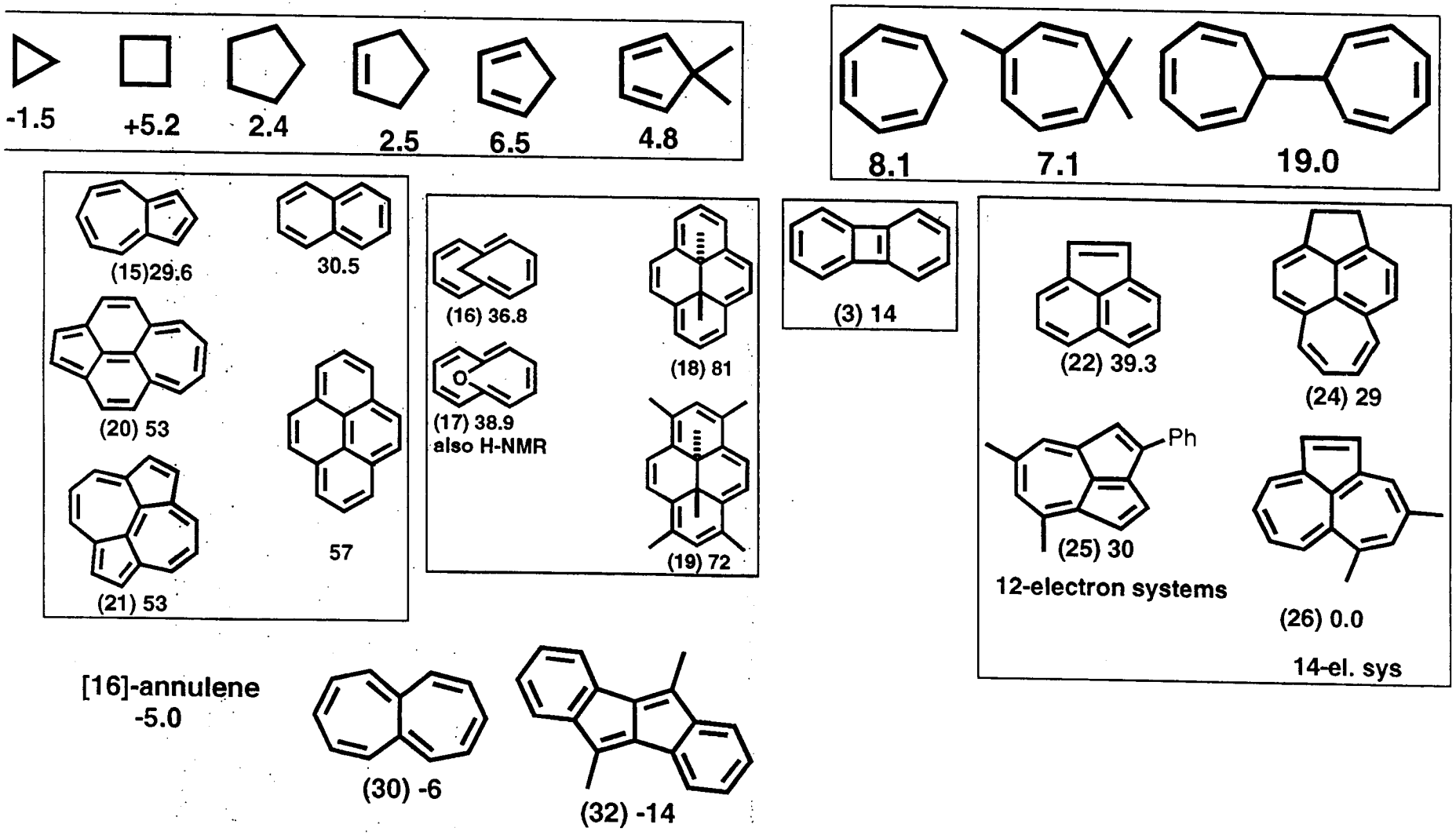
Table I. Diamagnetic Exaltation Data[a]

Compound	χ_M	$\chi_{M'}$	Λ
Nonaromatic Compounds			
Cyclopentane	59.2[b]	56.8	2.4
Cyclopentene	49.5 ± 0.5[k]	47.0	2.5
Cyclopentadiene (1)	44.5[b,k]	38.0	6.5
5,5-Dimethylcyclopentadiene (2)	67.5 ± 0.6[k]	62.7	4.8
Cyclohexane	68.1[b]	68.1	0.0
Cyclohexene	57.5[b]	58.3	−0.8
1,3-Cyclohexadiene	48.6[b]	49.3	−0.7
1,4-Cyclohexadiene	48.7[b]	48.5	0.2
Cycloheptane	78.9 ± 0.7[k]	79.5	−0.6
Cycloheptene	69.3 ± 0.6[k]	69.7	−0.4
1,3-Cycloheptadiene	61.0 ± 0.6[k]	60.7	0.3
1,4-Cycloheptadiene	61.0 ± 0.4[k]	59.9	1.1
1,3,5-Cycloheptatriene	59.8 ± 1.0[k]	51.7	8.1
3,7,7-Trimethyl-1,3,5-cycloheptatriene	95.6 ± 0.4[k]	88.5	7.1
7,7′-Bis(cycloheptatrienyl)	119 ± 3[k]	100.0	19.0
Cyclooctane	91.4[b]	90.8	0.6
Cyclooctene	80.5 ± 0.6[k]	81.0	−0.5
1,3-Cyclooctadiene	72.8 ± 0.8[k]	72.0	0.8
1,5-Cyclooctadiene	71.5 ± 0.7[k]	71.2	0.3
1,3,5-Cyclooctatriene	65.1 ± 0.8[k]	64.0	1.1
Cyclooctatetraene	53.9[i,k]	54.8	−0.9
Cyclododecene	127 ± 1[k]	126.4	0.6
Benzenoid Aromatic Compounds			
Benzene	54.8[b]	41.1	13.7
Toluene	66.1[b]	53.3	12.8
Styrene	68.2[b]	55.6	12.6
Indene	80.5[b,k]	61.4	19.1
Fluorene	110.5[c]	84.8	25.7
Triphenylmethane	166[e]	125	41
Stilbene	120[e]	82	28
1,4-Diphenylbutadiene	130[e]	106	24
Biphenyl	103.3[c]	77.1	26.2
p-Diphenylbenzene	152[c]	113	39
4,4′-Diphenylbiphenyl	201[c]	149	52
Biphenylene (3)	88 ± 3[k]	74	14
Naphthalene	91.9[b]	61.4	30.5
Anthracene	130.3[b]	81.7	48.6
Benzenoid Aromatic Compounds (*Continued*)			
Phenanthrene	127.9[b]	81.7	48.6
Tetracene (4)	168[b]	102	66
Chrysene (5)	167[b]	102	65
Pentacene (6)	205[b]	122	83
Dibenz[*a,h*]anthracene (7)	193[d]	122	71
Fluoranthene (8)	138[c]	96	42
Pyrene (9)	155[c]	98	57
Triphenylene (10)	157[c]	107	50
Perylene (11)	171[f]	121	50
Benzo[*a*]pyrene (12)	194[b]	119	75
Coronene (13)	243[b]	140	103
Ovalene (14)	354[b]	181	173
Nonbenzenoid Aromatic and Pseudoaromatic Compounds			
Azulene (15)	91.0[g]	61.4	29.6
1,6-Methano[10]annulene (16)	111.9 ± 0.4[k]	75.1	36.8
1,6-Oxido[10]annulene (17)	108.0 ± 0.5[k]	69.1	38.9
trans-15,16-Dimethyl-15,16-dihydropyrene (18)	210 ± 15[k]	129	81
1,3,6,8,15,16-Hexamethyl-15,16-dihydropyrene (19)	250 ± 20[k]	178	72
Acepleiadylene (20)	155 ± 5[k]	98	53
Dicyclopenta[*ef,kl*]heptalene (21)	151 ± 4[k]	98	53
Acenaphthylene (22)	111.6[c]	72.3	39.3
Acenaphthene (23)	109.3[b]	82.4	26.9
Acepleiadiene (24)	135 ± 3[k]	106	29
2-Phenyl-5,7-dimethylpleiapentalene (25)	179 ± 4[k]	149[l]	30
3,5-Dimethylaceheptalene (26)	112 ± 3[k]	112	0.0
Pentafulvene (27)	43.0[h]	41.9	1.1
Cyclooctatetraene (28)	53.9[i,k]	54.8	−0.9
[16]Annulene (29)	105 ± 2[k]	110	−5
Heptalene (30)	72 ± 7[k]	78.2	−6
Heptafulvalene (31)	94 ± 3[k]	92.0	2
9,10-Dimethyldibenzopentalene (32)	132[j]	146[l]	−14
7,7-Dimethylbenzofulvene	105[j]	103[l]	2
7-Phenylbenzofulvene	131[j]	130[l]	1

[a] All values of χ_M, $\chi_{M'}$, and Λ are given in units of -10^{-6} cm^3 mol^{-1}. The values of $\chi_{M'}$ are not corrected for "ring-current diamagnetism." [b] G. W. Smith, "A Compilation of Diamagnetic Susceptibilities," General Motors Corporation Research Report, GMR-317, 1960. [c] G. W. Smith, "Supplement to GMR-317," GMR-396, 1963. [d] K. Lonsdale and K. S. Krishnan, *Proc. Roy. Soc.* (London), **A156**, 597 (1936). [e] K. S. Krishnan and S. Bannerjee, *Phil. Trans. Roy. Soc.* (London), **A234**, 265 (1935). [f] H. Shiba and G. Hazato, *Bull. Chem. Soc. Japan*, **22**, 92 (1949). [g] W. Klemm, *Ber.*, **90**, 1051 (1957). [h] J. Thiec and J. Weimann, *Bull. Soc. Chim. France*, 177 (1956). [i] S. Shida and S. Fujii, *Bull. Chem. Soc. Japan*, **24**, 173 (1951). [j] E. D. Bergmann, J. Hoarau, A. Pacault, B. Pullman, and A. Pullman, *J. Chim. Phys.*,

Hyp J. Dauben, Jr., James D. Wilson, and John L. Laity *JACS*, **1969**, *91*, 1991

Criteria of aromaticity. Magnetic criteria.

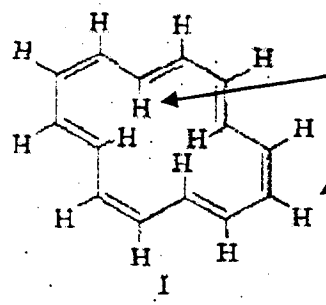


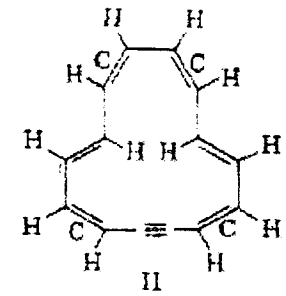
Hyp J. Dauben, Jr., James D. Wilson, and John L. Laity *JACS*, **1969**, *91, 1991*

Criteria of aromaticity. Magnetic criteria.

C. NMR Chemical Shifts

Later. Low temp?
0.61, 7.9ppm





5.58ppm

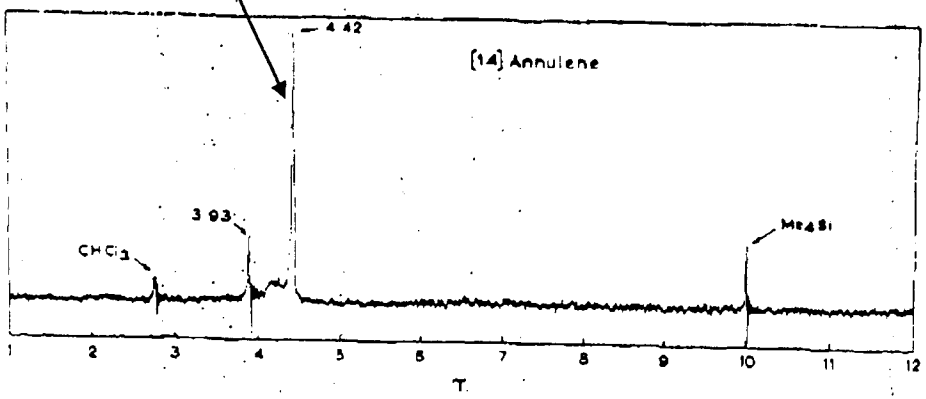


Fig. 2.—N.m.r. spectrum of [14]annulene (I) (60 Mc./sec.; deuteriochloroform solution).

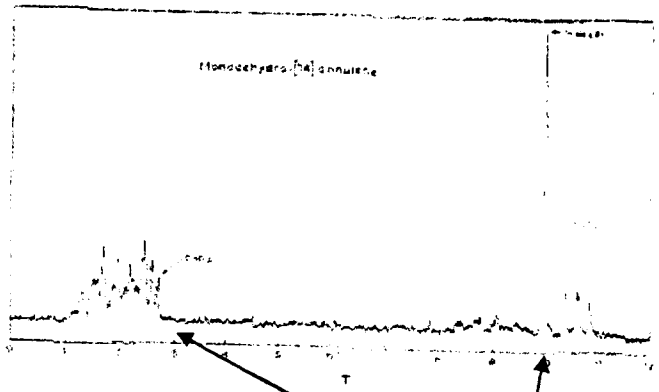


Fig. 3.—N.m.r. spectrum of monodehydro-[14]annulene (e.g., II) (60 Mc./sec.; deuteriochloroform solution).

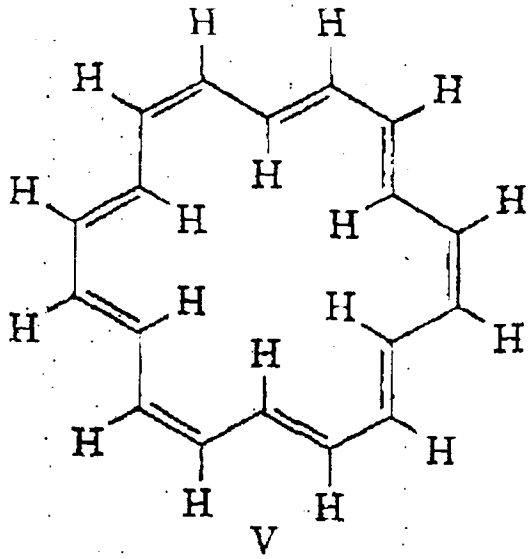
Area ratio 5:1

F.Sondheimer *Acct.Chem.Res*, **1972**, *5*, 81

F.Sondheimer et. al. *JACS*, **1962**, *84*, 4307

Criteria of aromaticity. Magnetic criteria.

C. NMR Chemical Shifts



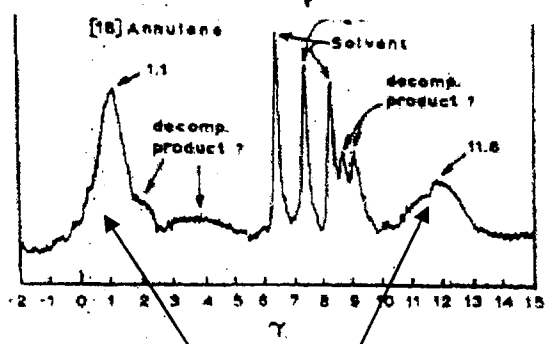
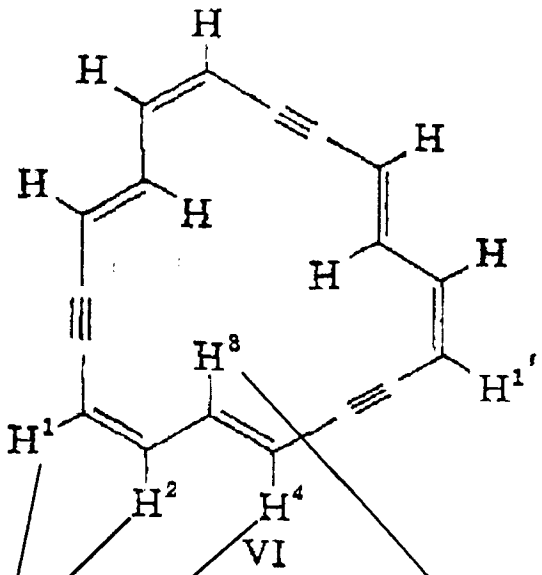


Fig. 4.—N.m.r. spectrum of [18]annulene (V) (60 Mc./sec.; perdeuteriotetrahydrofuran solution).

Area ratio 2:1



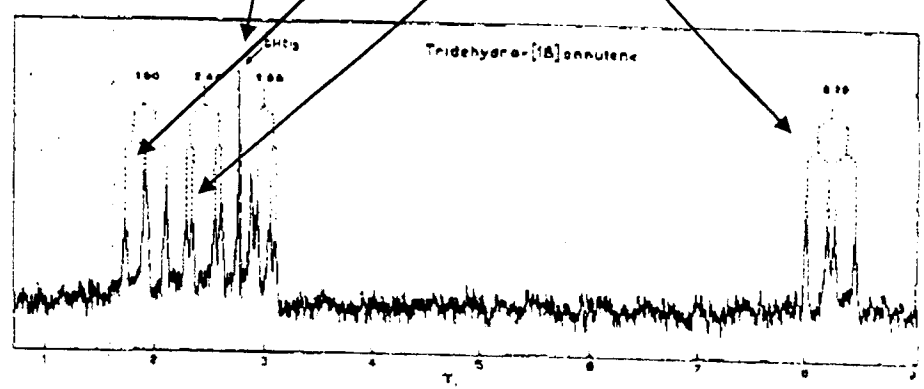
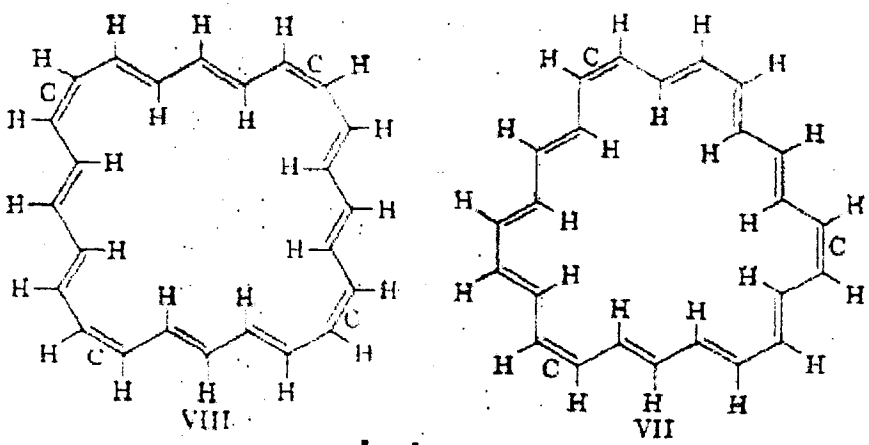


Fig. 5.—N.m.r. spectrum of tridehydro-[18]annulene (VI) [60 Mc./sec. (Varian A60 spectrometer); deuteriochloroform solution].

F.Sondheimer et. al. *JACS*, **1962**. *84*, 4307

Criteria of aromaticity. Magnetic criteria.

C. NMR Chemical Shifts



Later.
12; 5 ppm

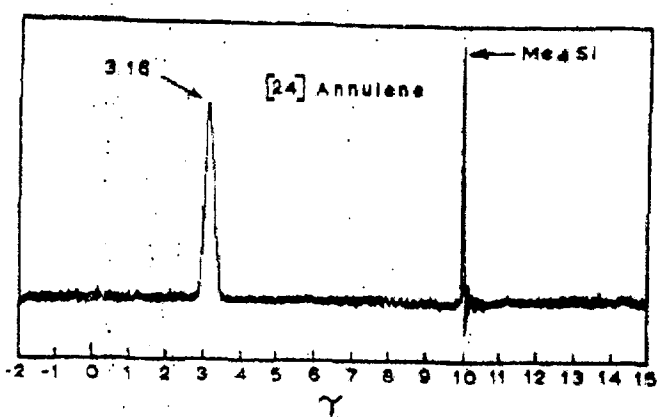
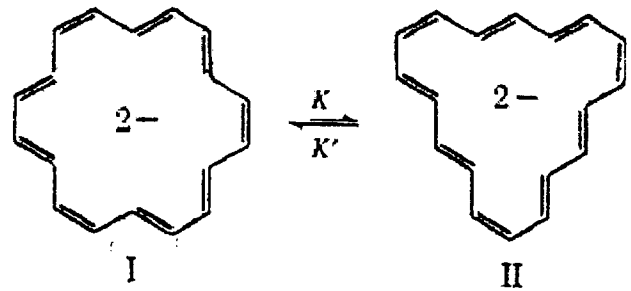
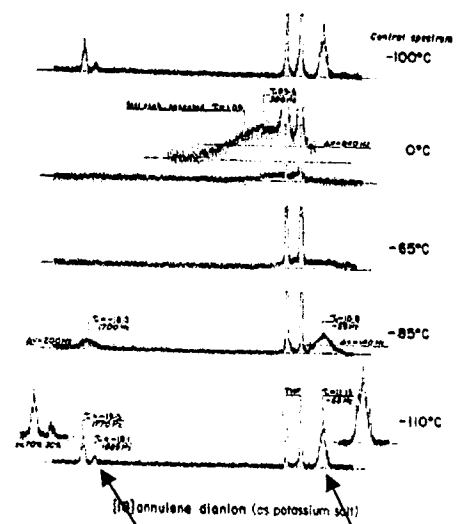


Fig. 6.—N.m.r. spectrum of [24]annulene (*e.g.*, VII) (56.4 Mc./sec.; deuteriochloroform solution).



[18]-219-annulene dianion



[18]annulene dianion (cs potassium salt)

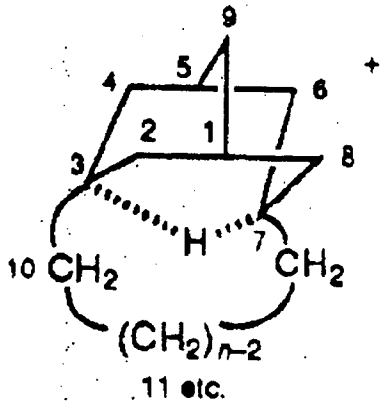
Figure 2. Temperature dependence of the ^{1}H-nmr spectrum (at 60 MHz) of the dianion of [18]annulene (as the potassium salt).

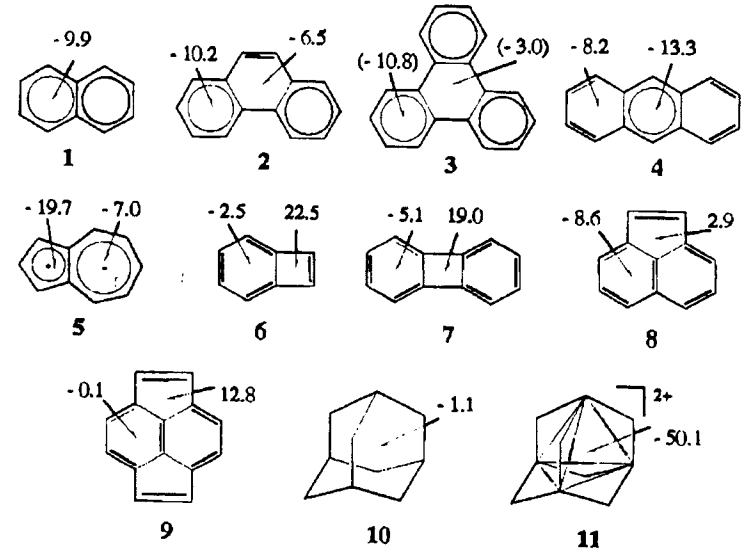
28 ppm, -1ppm

F.Sondheimer et. al. *JACS*, **1962**, *84*, 4307; *ibid*, **1973**, *95*, 7337

Criteria of aromaticity. Magnetic criteria.

C. NMR Chemical Shifts





n=7	δ=-5.64
n=8	δ=-4.28
n=9	δ=-1.46
n=10	δ=+0.07

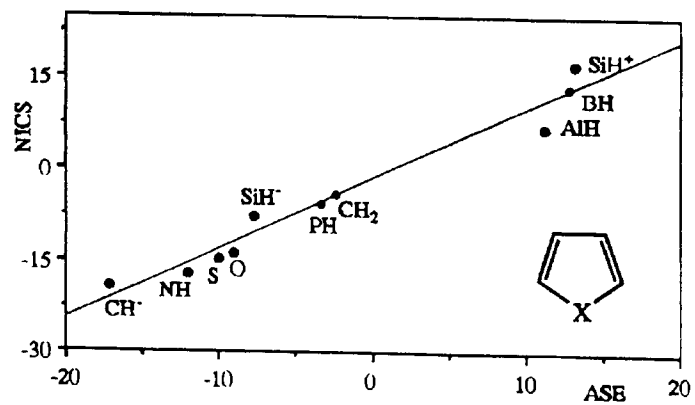
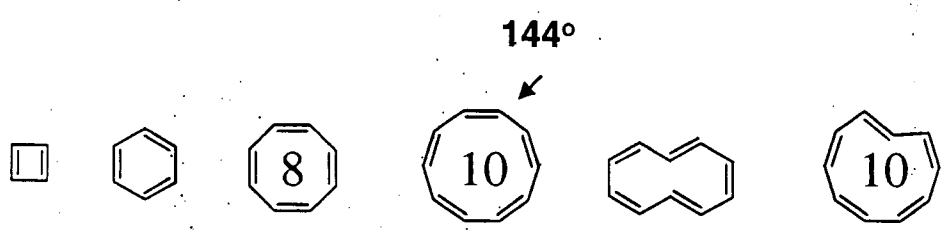
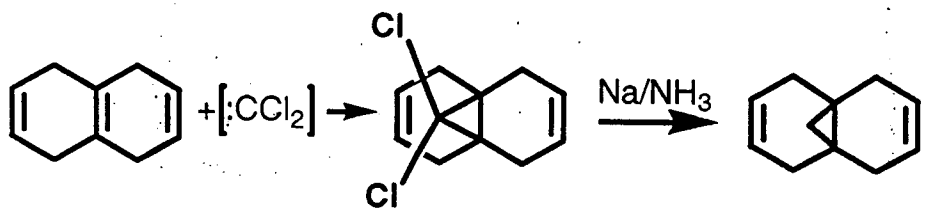


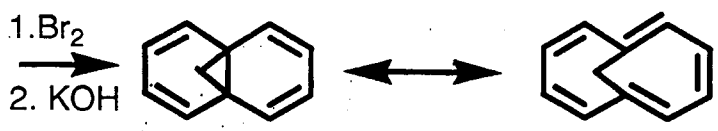
Figure 1. Plot of NICSs (ppm) vs the aromatic stabilization energies (ASEs, kcal/mol)[5a] for a set of five-membered ring heterocycles, C_4H_4X (X = as shown) (cc = 0.966).

T. S. Sorensen* and S. M. Whitworth *JACS*, **1990**, *112*, 8135
Paul von Rague Schleyer et.al. *JACS*, **1996**, *118*, 6317

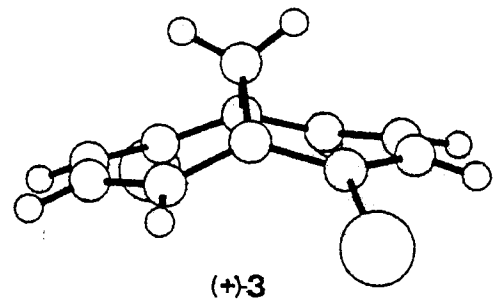
Aromaticity. Annulenes.





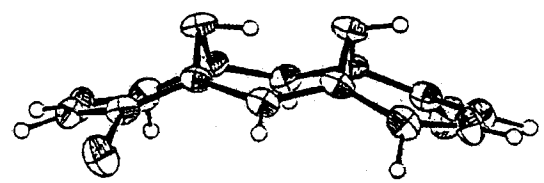


6.8-7.5ppm, A_2B_2-system, 8H
-0.5ppm, s, 2H
XRay: 1.37-1.42A, nonplanar

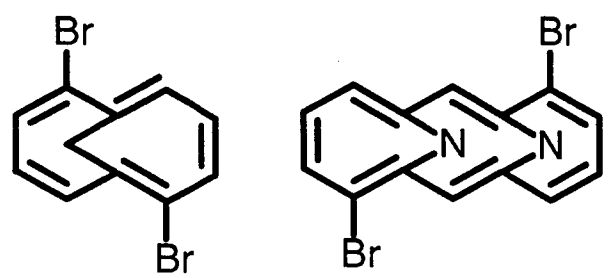


(+)-3

chiral!

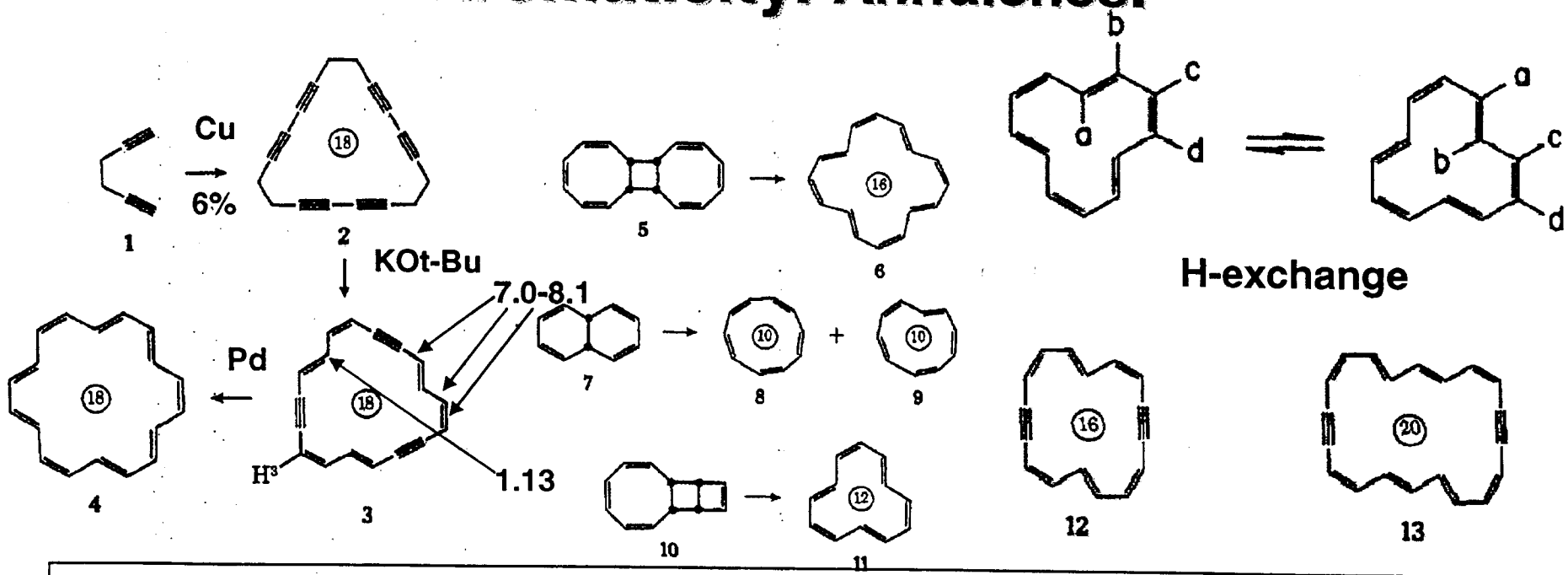


(+)-9



D.E.Vogel;H.D.Roth *Angew.Chem.Int.Ed.Engl.*, **1964,** *3,* 228
Vogel, E. et.al. *Monatshefte fur Chemie,* **1986,** *117,* 255

Aromaticity. Annulenes.

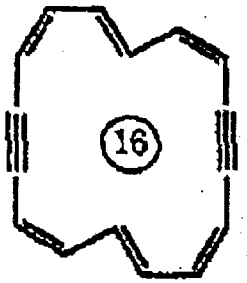


Low temp. H-NMR:							
n	10	12	14	16	18	22	24
Inner	5.7-5.8	8	-0.61	10.56	-2.99	-0.4-1.2	11.2-12.9
Outer	5.7-5.8	6	7.88	5.33	9.28	8.5-9.6	4.7
Planarity (X-RAY)			not	fig	fig		

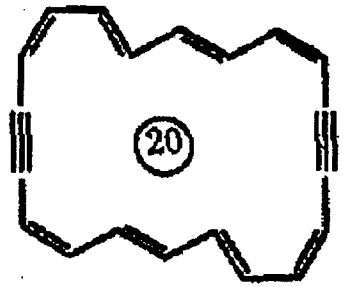
[20]- and [30]-annulenes were not homogenious

F.Sondheimer *Acct.Chem.Res.*, **1972**, *5*, 81

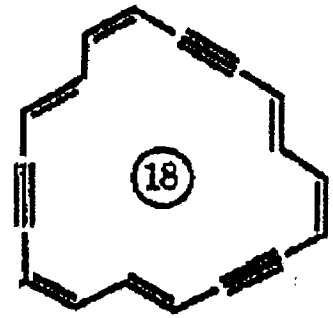
Aromaticity. Dehydroannulenes.



12



13



3

H-NMR of dehydroannulenes

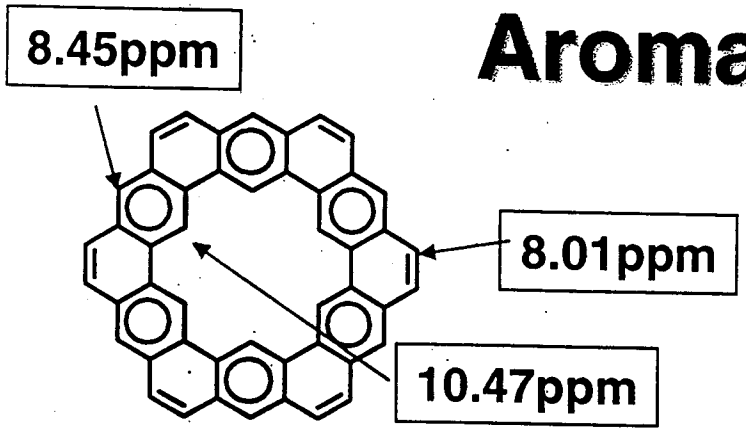
n	12	14	16	18	20	22	24	26	30
-tropic	para	dia	para	dia	para	dia	para	not	not

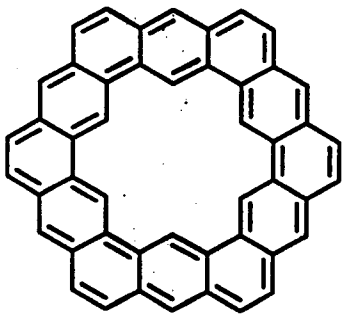
[28]-dehydroannulene has too low solubility

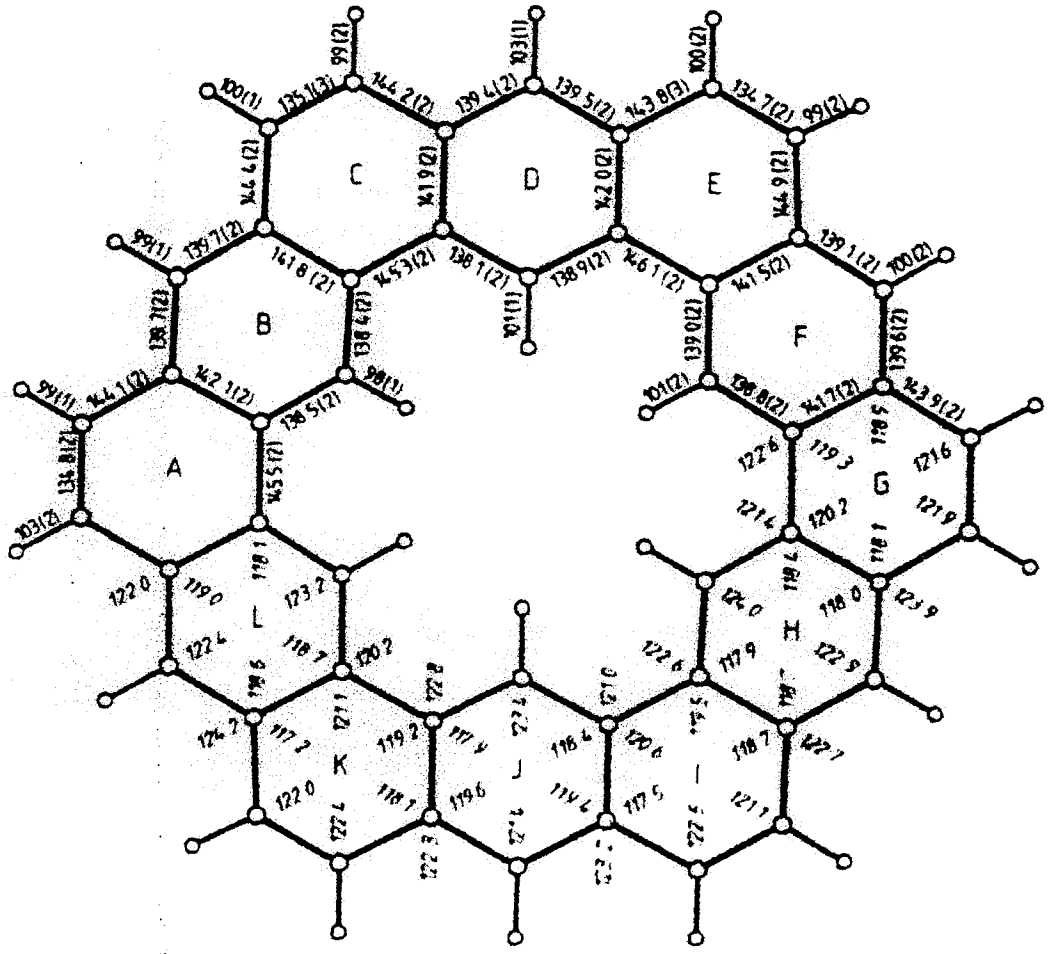
[18]-annulene –NO2, MeCO, Br, CHO
[14]- and [12]-bisdihydroannulenes were electrophilically substituted

F.Sondheimer *Acct.Chem.Res.*, 1972, *5*, 81

Aromaticity. Kekulene.

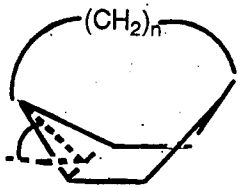






H.A. Staab et.al. *Chem.Ber.*, **l983,** *116,* 3504;**ibid,** 3487

Aromaticity. Cyclophanes



Benzene		HSE_{calc}=-28.1kcal/mol
n=5	φ=23.7	HSE_{calc}=+50.1 kcal/mol
n=6	φ=18.6	HSE_{calc}=+26.3 kcal/mol
n=7	φ=14.2	HSE_{calc}=+12.9 kcal/mol
n=8	φ= 8.4	HSE_{calc}=+ 6.3 kcal/mol
Benzene 160°		=-13.1kcal/mol

Energetic	no?
Structural(planar)	no
Structural(bond alt)	yes
NMR	yes

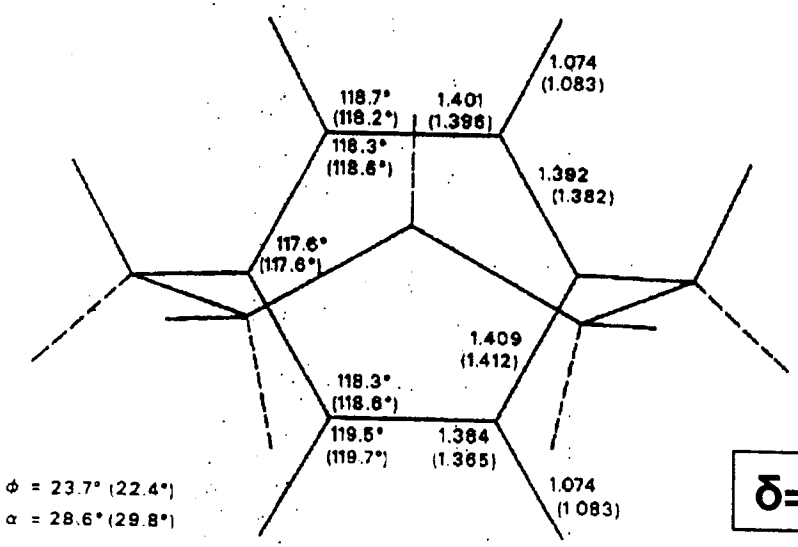


Figure 3. The theoretical molecular structure of [5]paracyclophane based on the double-ζ (DZ) self-consistent-field (SCF) method. This sketch shows only the geometrical parameters for the benzene ring portion of the molecule. Refer to the supplementary material (Table Is) for a complete set of geometrical parameters. In parentheses is given the minimum basis structure of ref 25.

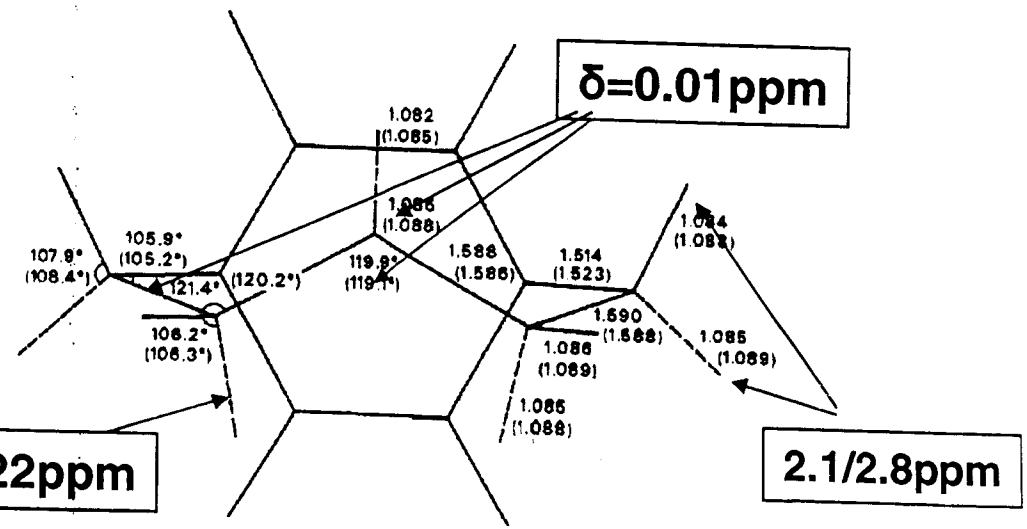
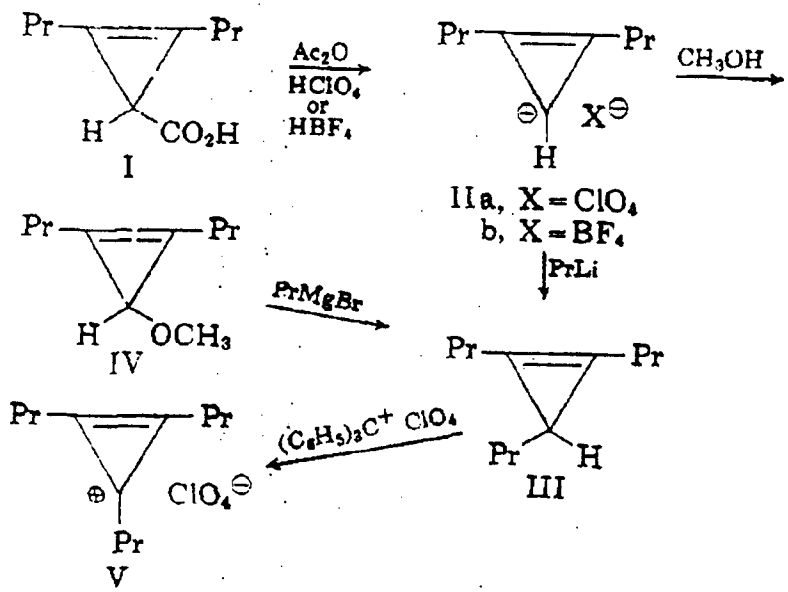


Figure 4. The theoretical molecular structure of [5]paracyclophane based on the double-ζ (DZ) self-consistent-field (SCF) method. Shown here are geometrical parameters for the five methylene groups [i.e., $(CH_2)_5$] bridging the para positions of the benzene ring. Refer to the supplementary material (Table Is) for a complete set of geometrical parameters. In parentheses is given the minimum basis set structure of ref 25.

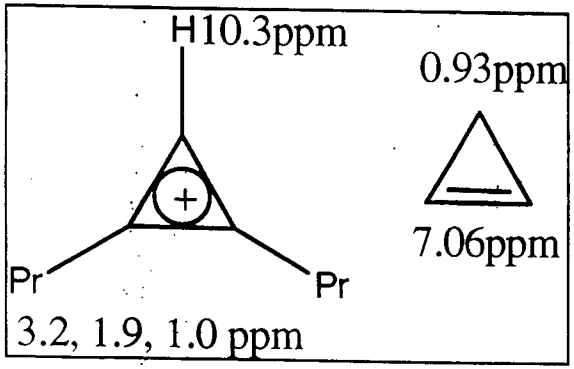
H.F.Schaefer III et. al. *JACS.*, **1987**, *109*, 2902

Friedrich Bickelhaupt et.al. *JACS*, **1985**, *107*, 3716

Aromaticity. Aromatic ions.



All Pr are equal by NMR



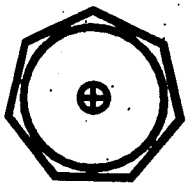
Breslow,R. et.al. *JACS*, **1962**, *84*, 3168;

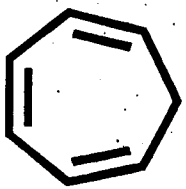
$pK_R{}^+$'s OF SOME CYCLOPROPENYL CATIONS

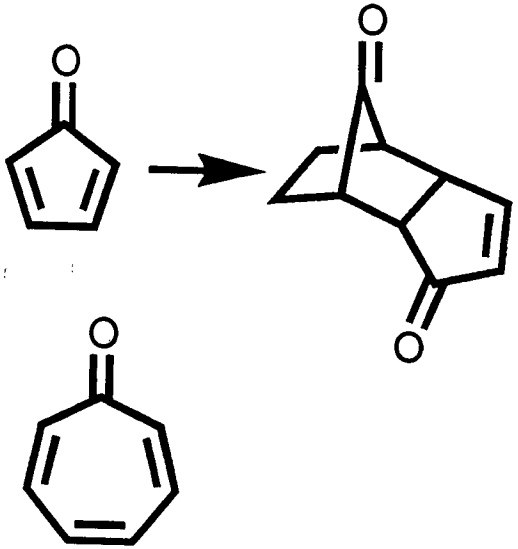
Compound	Medium[a]	Method[b]	$pK_R{}^+$
Dipropylcyclopropenyl perchlorate (IIa)	A	a	2.7
Tripropylcyclopropenyl perchlorate (V)	A	a	7.2
Trianisylcyclopropenyl bromide[3]	A	a	6.5
	B	b	6.4
Dianisylphenylcyclopropenyl bromide[3]	A	a	5.2
	B	b	5.2
Triphenylcyclopropenyl bromide[3]	A	a	3.1
	B	b	2.8
Diphenylcyclopropenyl bromide[4]	B	b	−0.67
	C	b	0.32
Propyldiphenylcyclopropenyl fluoroborate (VII)	B	b	3.8

[a] A, 50% aqueous acetonitrile; B, 23% aqueous ethanol C, water. [b] a, potentiometric titration; b, spectrophotometric titration.

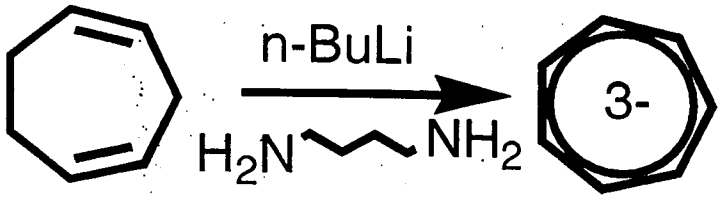
Aromaticity. Aromatic ions.



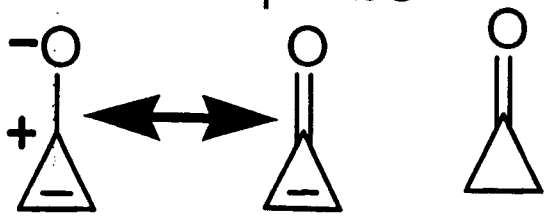




pKa=10^{-39} **pKa=10^{-16}**



Stable<Mp=-29C



Polymerizes

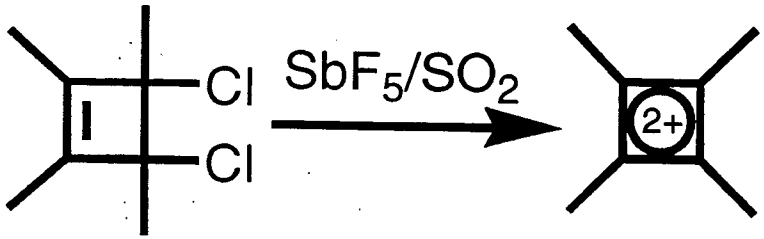
Ogliaruso, M.A. et.al. *Chem.Rev.*, **1965**, *65*, 261

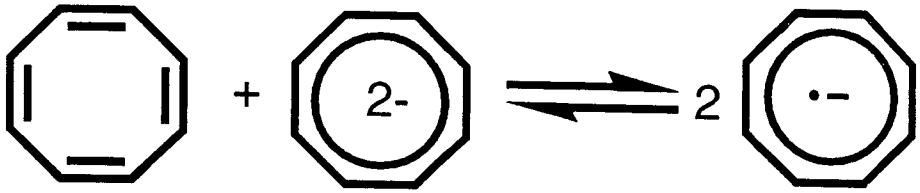
From T.H.Lowry;K.S.Richardson *Mechanism and theory in Org.Chem.* HarperCollins: New York, **1987**, p.50

Bates, R.B. et.al. *JACS*, **1977**, *99*, 6126;

Breslow,R. et.al. *JACS*, **1962**, *84*, 3168;

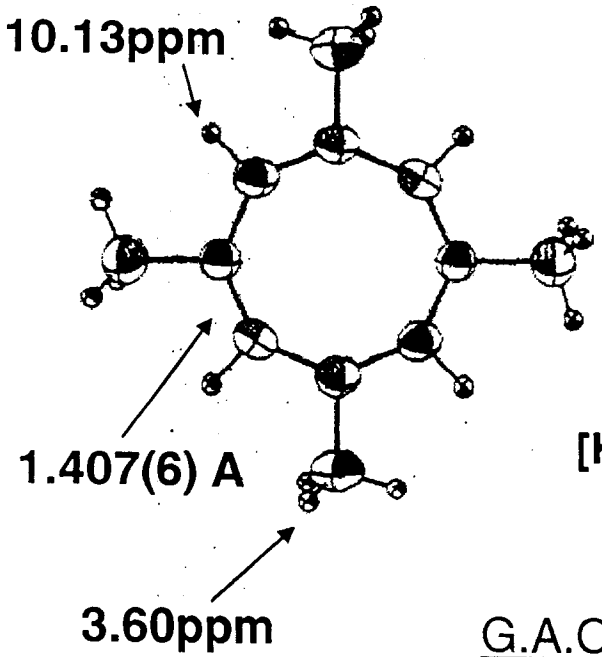
Aromaticity. Aromatic ions.

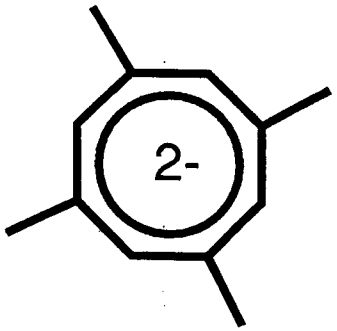


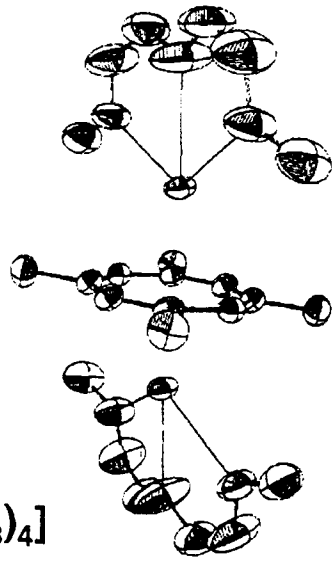


δH =3.68ppm
δC_{ring}=-14(CS_2)
δCS_2=190ppm

δH =5.78ppm







$[K((CH_3OCHiCH_2)_2O)]_2[C_8H_4(CH_3)_4]$

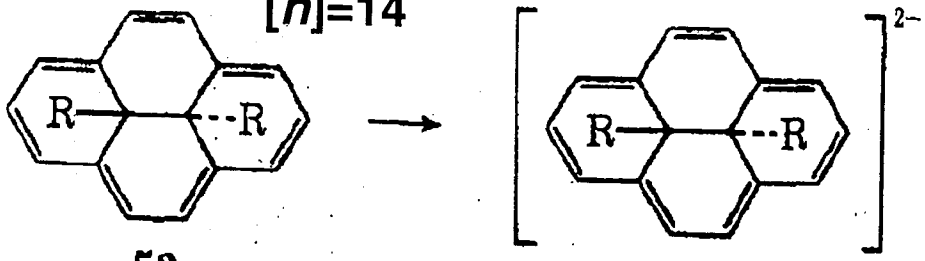
G.A.Olah et.al. *JACS*, **1969**, *91*, 3667

T.J.Katz. *JACS*, **1960**, *82*, 3784, 3385

K.N.Raymond et.al *JACS*, **1974**, *96*, 1348

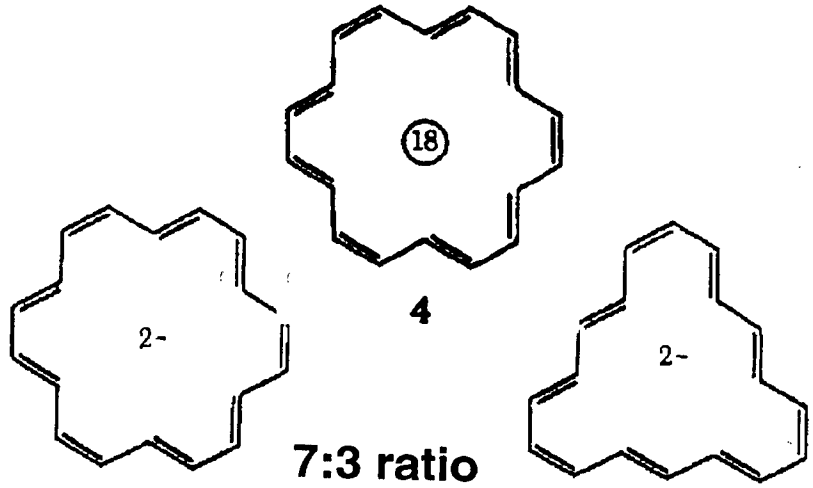
Aromaticity. Aromatic ions.

[*n*]=14



52 53

R=Me; H_{Me} from -4.25 to 21ppm
H_{out} 8-8.7 to -3-4ppm

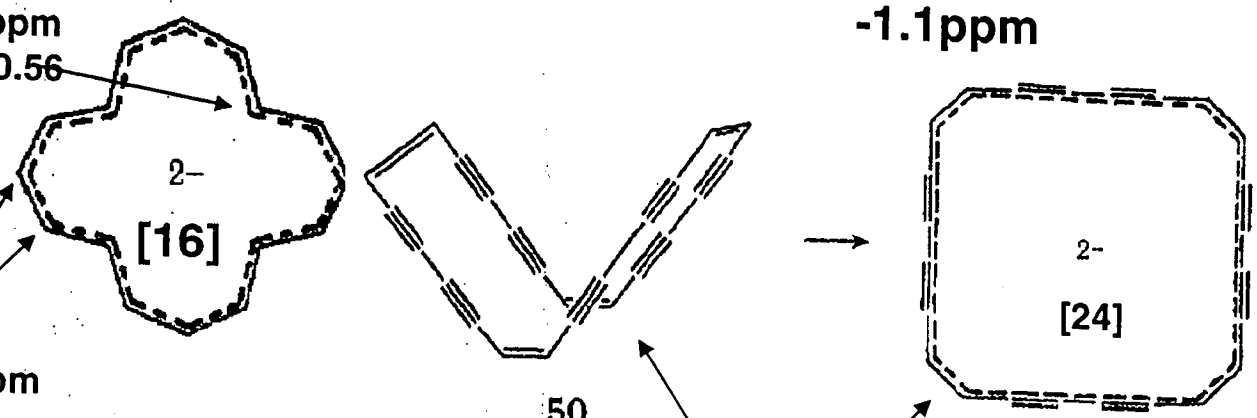


4 54 55

7:3 ratio
29.5, 28.1ppm
-1.1ppm

-8.2ppm
vs.10.56

Stable 100°C 2days



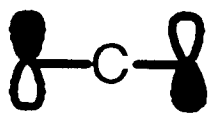
8.3,7.4ppm
vs. 5.33

50 51

H-NMR spectra similar

F.Sondheimer *Acct.Chem.Res.*, **1972**, *5*, 81

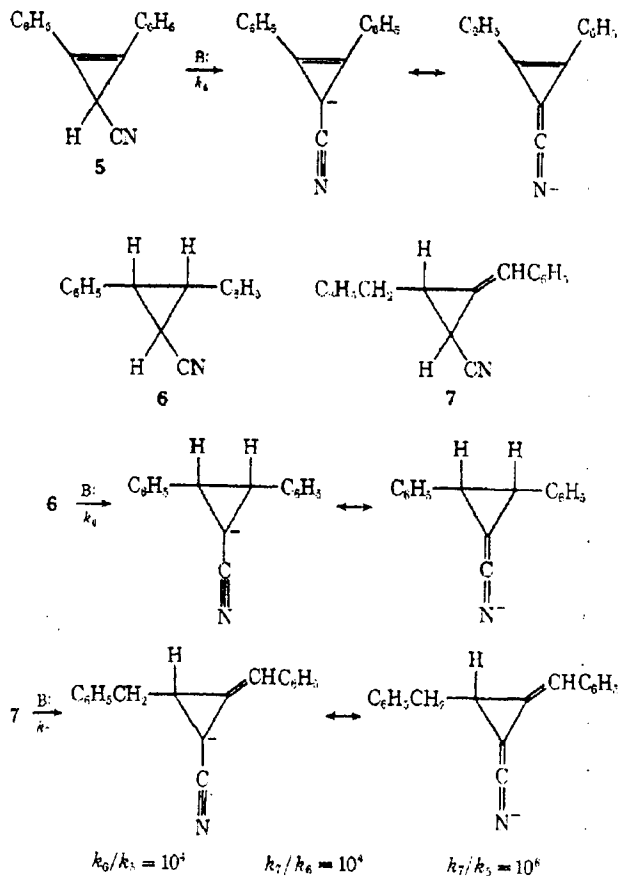
Antiaromaticity



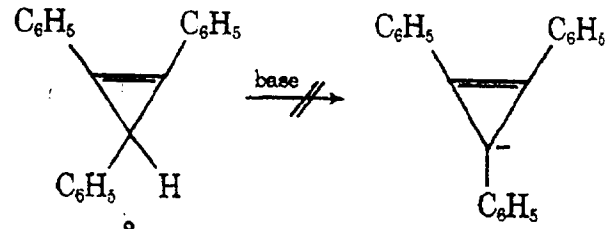
ψ_2

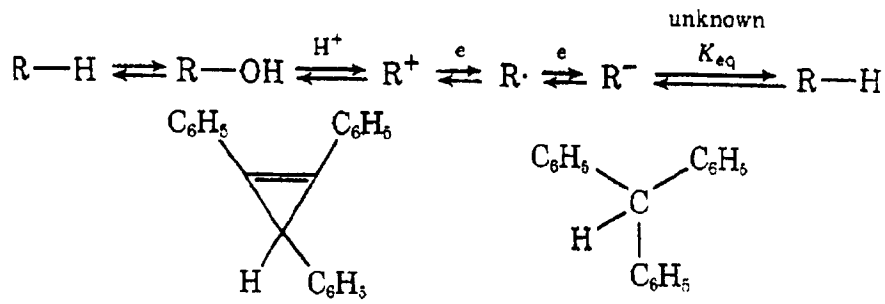
ψ_1

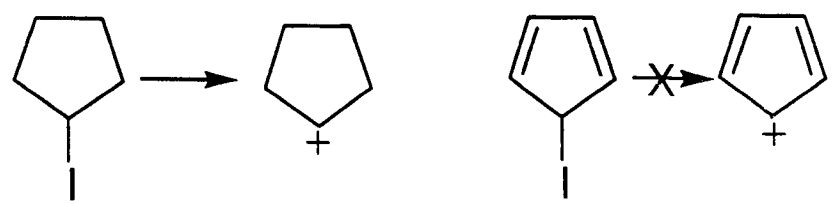
Kinetic acidity study



Thermodinamic acidity study







R.Breslow *Acct.Chem.Res.*, **1973**, *6*, 393
R.Breslow, W.Chu, *JACS*, **1973**, *95*, 411

Antiaromaticity

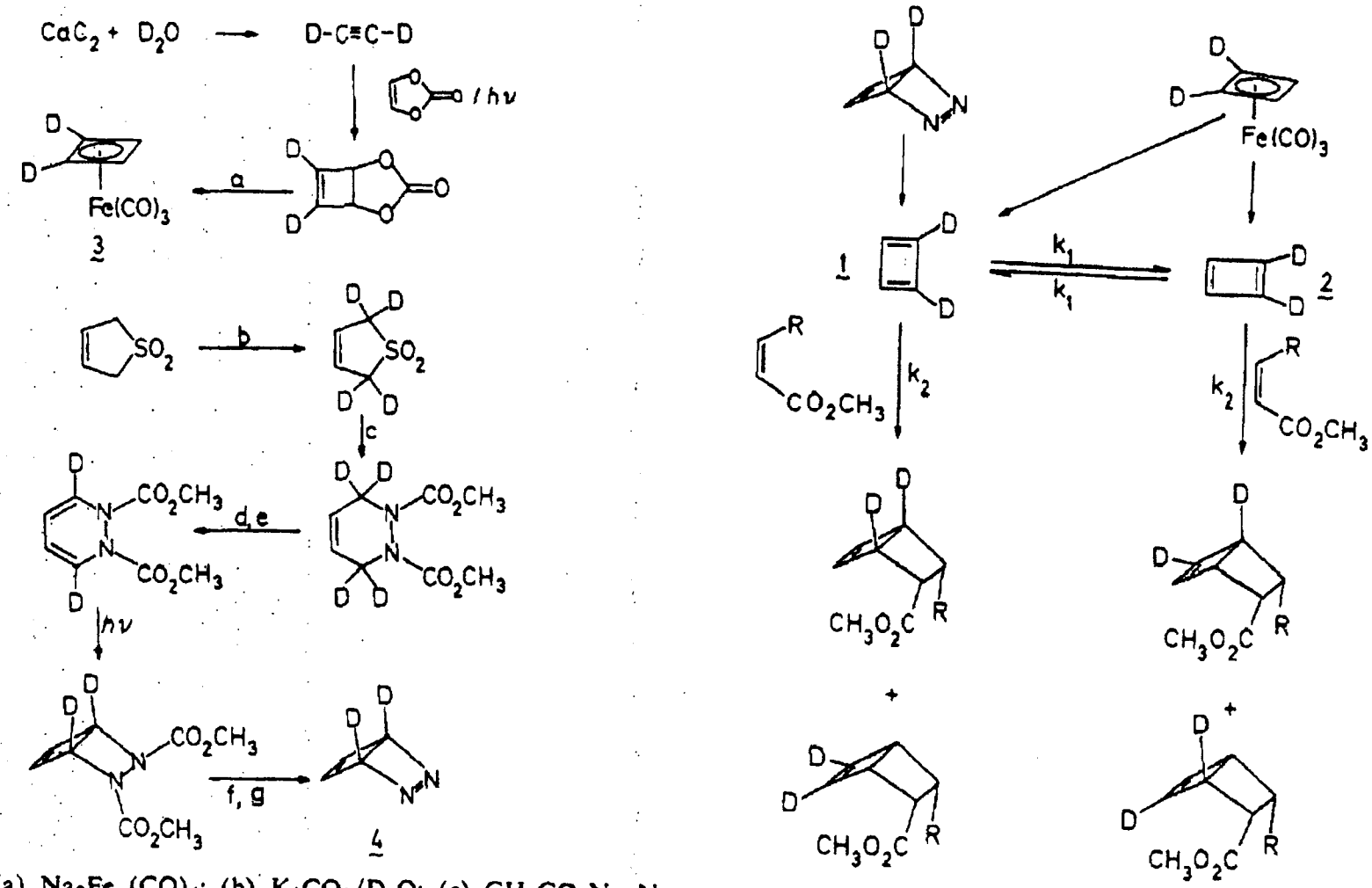


Figure 1. (a) $Na_2Fe(CO)_4$; (b) K_2CO_3/D_2O; (c) $CH_3CO_2N{=}N{-}CO_2CH_3/\Delta$; (d) *N*-bromosuccinimide; (e) 2,6-lutidine; (f) $KOBu^t/Me_2SO$; (g) $Pb(OAc)_4$.

B.K.Carpenter *JACS*, **1980**, *102*, 4272

Antiaromaticity

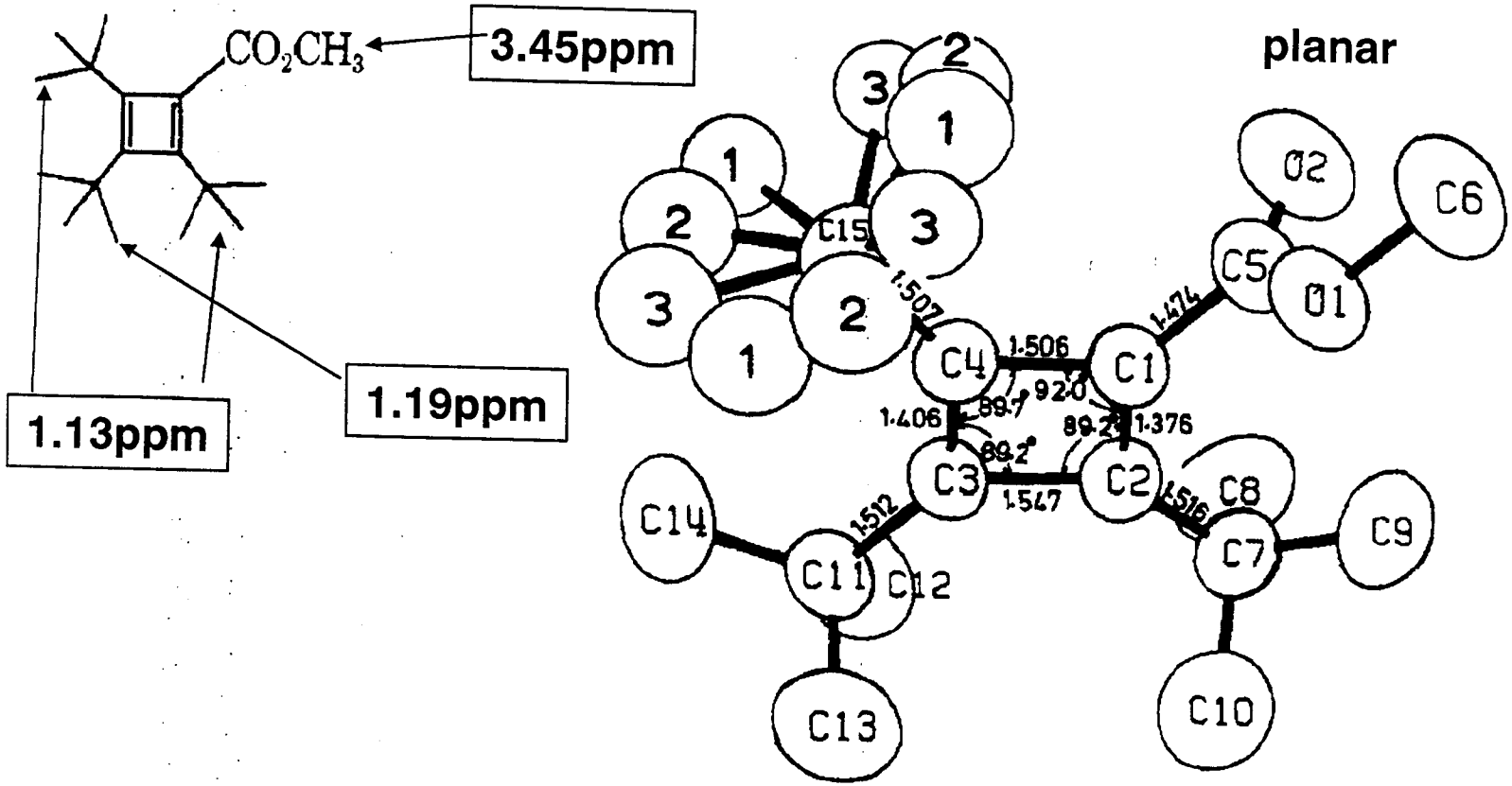
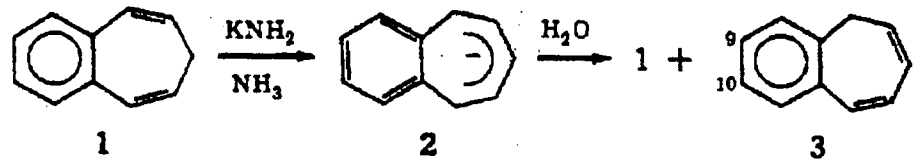


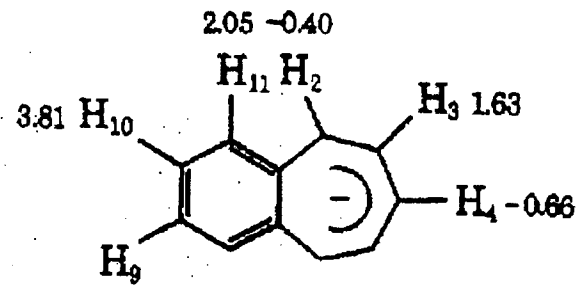
Figure 1. Methyl tri-*tert*-butyl[4]annulenecarboxylate. Selected bond distances and angles are given and the estimated standard deviations of the bond distances and angles are 0.005 Å and 0.3°, respectively. The three sites (occupancies 0.51, 0.32, 0.17) of the disordered methyl groups bonded to C15 are designated as 1, 2, and 3, respectively.

S. Masamune et. al *JACS*, 1975, *97*, 1973

S. Masamune et. al *JACS*, 1973, *95*, 8481

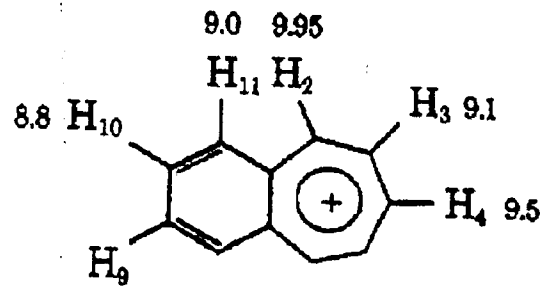
Antiaromaticity





2

J_{23} = 10.8 Hz
J_{34} = 8.2
$J_{9,10}$ = 8.0
$J_{10,11}$ = 6.4
$J_{9,11}$ = 2.2



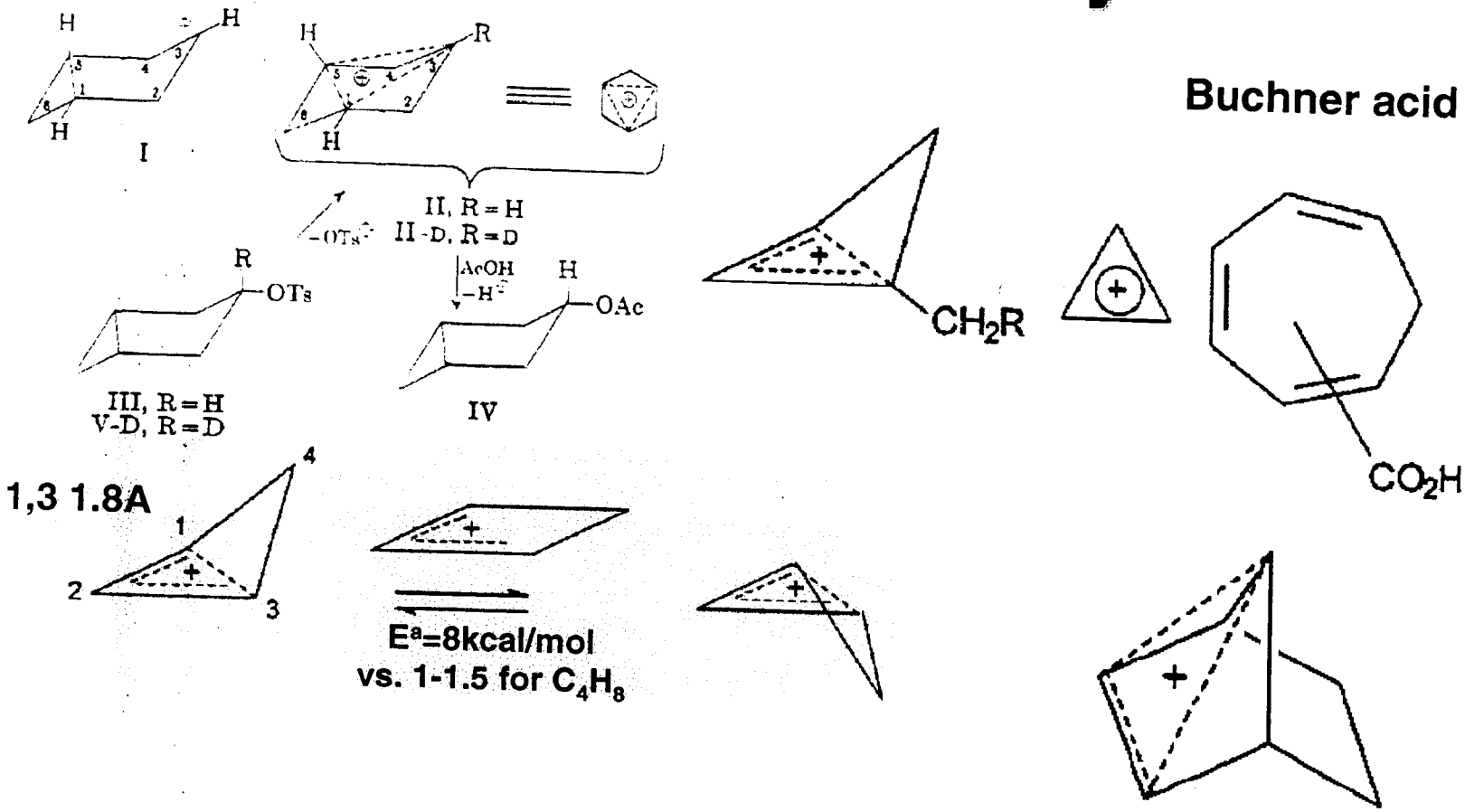
4

J_{23} = 10.2 Hz
J_{34} = 9.8
$J_{9,10}$ = 6.0
$J_{10,11}$ = 8.5
$J_{9,11}$ = 1.3

Figure 1. Nmr spectral data for the (potassium) benzocycloheptatrienyl anion (2) in ammonia-d_3 at −50° (with trimethylamine ($\delta_{TMS}^{NH_3}$ 2.135) as internal standard) and the benzocycloheptatrienyl cation[13] (4) in acetonitrile-d_3 at 32° (with TMS as internal standard).[13a]

Staley, S.W. *JACS*, **1973**, *95*, 3382

Homoaromaticity

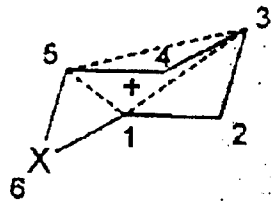


Winstein,S. *JACS*, **1959**, *81*, 6524

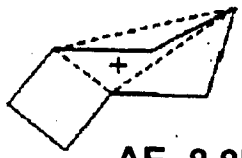
Applequist, D.E.;Roberts,J.D. *JACS*, **1956**, *78*, 4012

Doering W.v.E. et.al. *JACS*, **1956**, *78*, 5448

Homoaromaticity



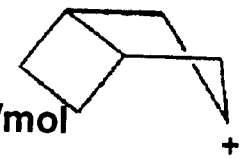
35 X = NH
36 X = O
37 X = BH



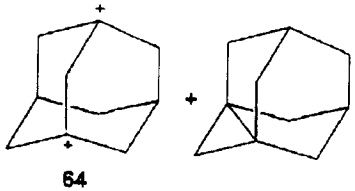
ΔE=8.8kcal/mol

38

More stable

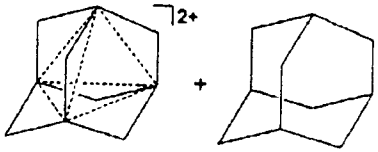


39



64

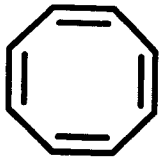
ΔE=47kcal/mol



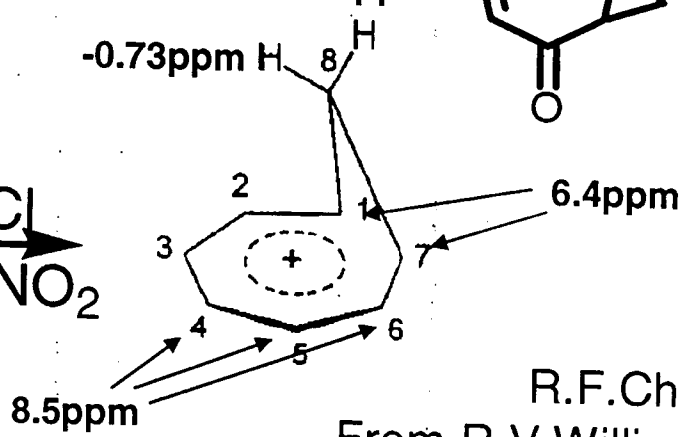
63

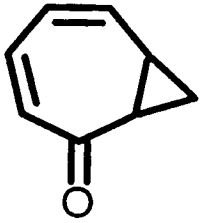
#	35	36	37	38
1,5(A)	1.74	1.71	2.00	1.65

1.400+/-0.004A
1,7=2.0A
ΔE=22.3kcal/mol
2-6: 8.6ppm
1,7: 6.6ppm

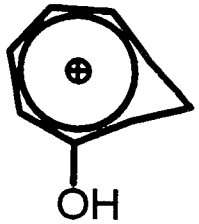


+ $SbCl_5$ $\xrightarrow[MeNO_2]{HCl}$





$\xrightarrow[MeNO_2]{HCl/SbCl_5}$



$SbCl_6^-$

R.F.Childs et.al. *JACS*, **1982,** *104, 2452*
From R.V.Williams. *Chem.Rev.*, **2001,** *101*, 1185
R.Petit et.al. *JACS.*, **1962,** *84*, 2842

Homoaromaticity. Hydroxy-homotropyllium cation.

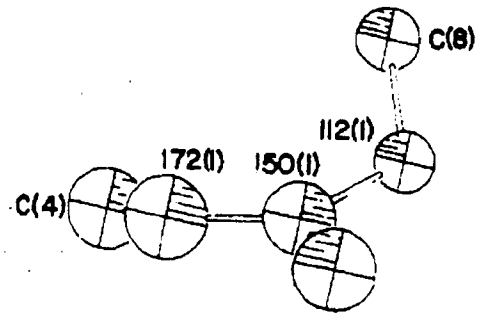


Figure 3. The cation $C_8H_8(OH)^+$ showing the dihedral angles between planes of atoms (temperature factors are isotropic for simplicity).

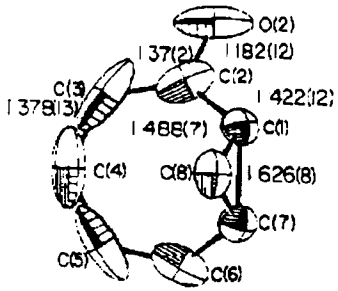


Figure 2. The cation $C_8H_8(OH)^+$ showing the atom numbering.

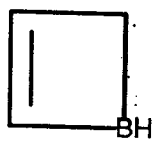
Table IV. Selected Interatomic Distances (Å) and Angles (Deg)

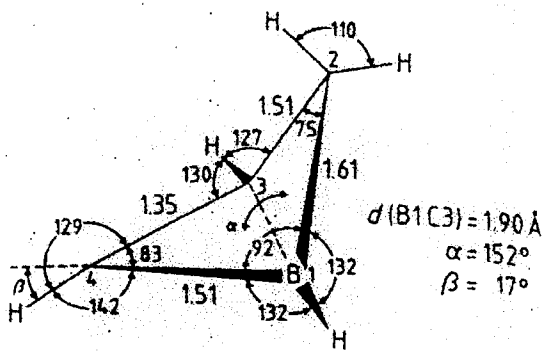
		Interatomic Distances			
Sb(1)–Cl(11)	2.363 (2)	Sb(1)–Cl(12)	2.350 (2)	Sb(2)–Cl(21)	2.365 (2)
Sb(2)–Cl(22)	2.365 (1)	C(1)–C(2)	1.422 (12)	C(2)–C(3)	1.368 (16)
C(3)–C(4)	1.378 (13)	C(1)–C(8)	1.488 (7)	C(1)–C(7)	1.626 (8)
C(2)–O(2)	1.182 (12)				
		Possible Hydrogen Bonds			
O(2)···Cl(22)[a]	3.292 (9)	O(2)···Cl(11)	3.15 (1)	O(2)···Cl(12)[b]	3.332 (9)
		Interatomic Angles			
Cl(11)–Sb(1)–Cl(12)	90.4 (1)	Cl(11)–Sb(1)–Cl(12)[a]	89.6 (1)	Cl(12)–Sb(1)–Cl(12)[a]	90.4 (1)
C(12)–Sb(1)–Cl(12)[c]	89.6 (1)	Cl(21)–Sb(2)–Cl(22)	90.3 (1)	Cl(21)–Sb(1)–Cl(21)[d]	89.7 (1)
Cl(22)–Sb(2)–Cl(22)[d]	90.1 (1)	Cl(22)–Sb(2)–Cl(22)[e]	89.9 (1)	C(8)–C(1)–C(2)	121.8 (3)
C(1)–C(2)–C(3)	128.9 (7)	C(2)–C(3)–C(4)	127 (1)	C(3)–C(4)–C(5)	130 (1)
C(7)–C(1)–C(2)	127.0 (7)	C(8)–C(1)–C(7)	56.9 (3)	C(1)–C(8)–C(7)	66.2 (4)
C(1)–C(2)–O(2)	115 (1)	C(3)–C(2)–O(2)	117 (1)		

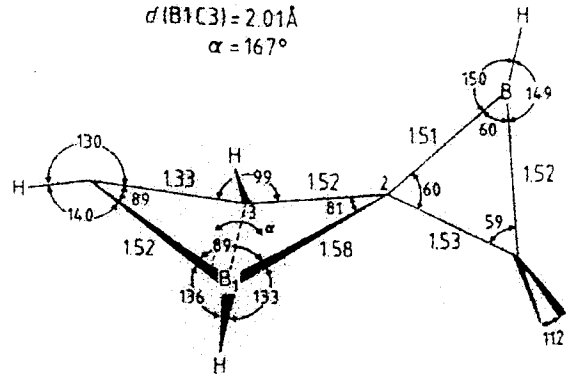
[a–f] Atoms are related to those given in Table II: *a*, $-x, y, -z$; *b*, $x, -y, z$; *c*, $-x, -y, -z$; *d*, $1-x, y, -z$; *e*, $1-x, 1-y, -z$; *f*, $x, 1-y, z$. C(5), C(6), and C(7) are related to atoms C(3), C(2), and C(1) respectively by *f*.

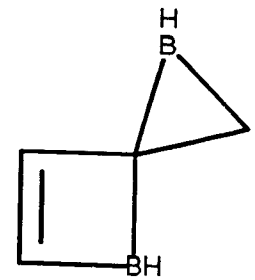
R.F.Childs et.al. *JACS*, **1982**, *104, 2452*

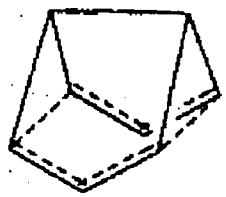
Homoaromaticity. Neutral molecules.



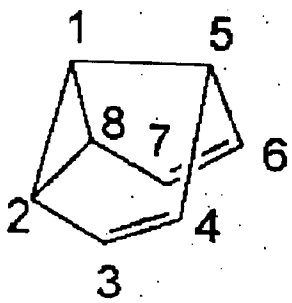








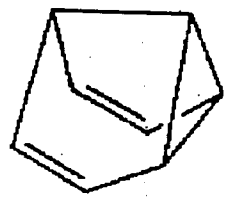
68c



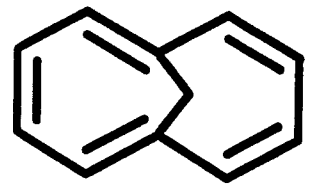
68a

$\rightleftharpoons$

ΔG‡=6kcal/mol



68b



P.v.R.Schleyer et.al. *Angew.Chem.Int.Ed.Engl.* **1984,** *23,* 370

Conclusions

- Definition of Aromaticity is not a simple matter
- Ring current is the major used manifestation of Aromaticity
- If a structure can be planar, it will be aromatic (4n+2 annulenes, n<6-8)
- If a structure can (or forced) to be planar, it can be antiaromatic (4n annulenes, n<6-8)
- Both are quantitative and it is proper to talk about degree of (anti-)aromaticity, rather than if it is aromatic or not

Appendix A.Structures of certain aromatic /pseudoaromatic compounds

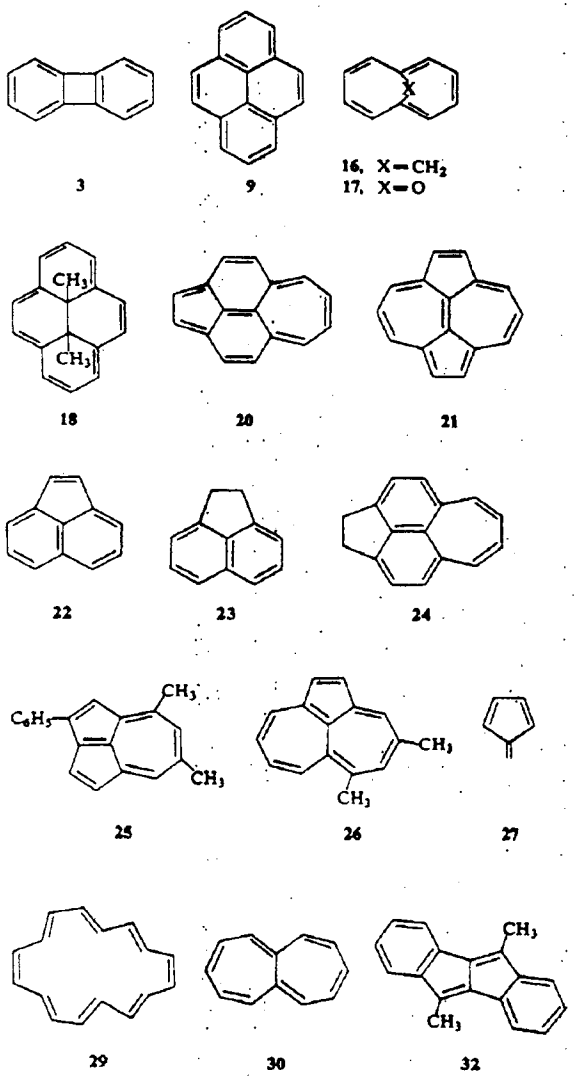
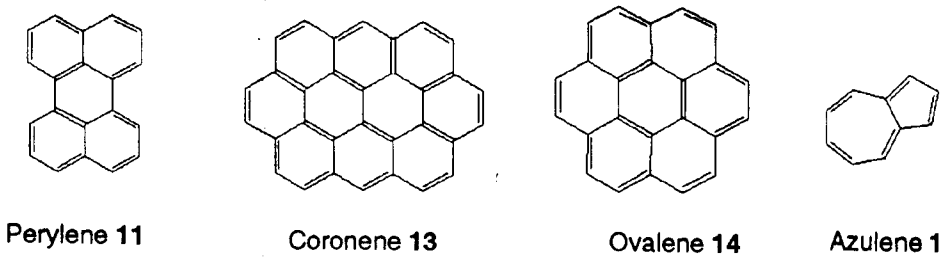


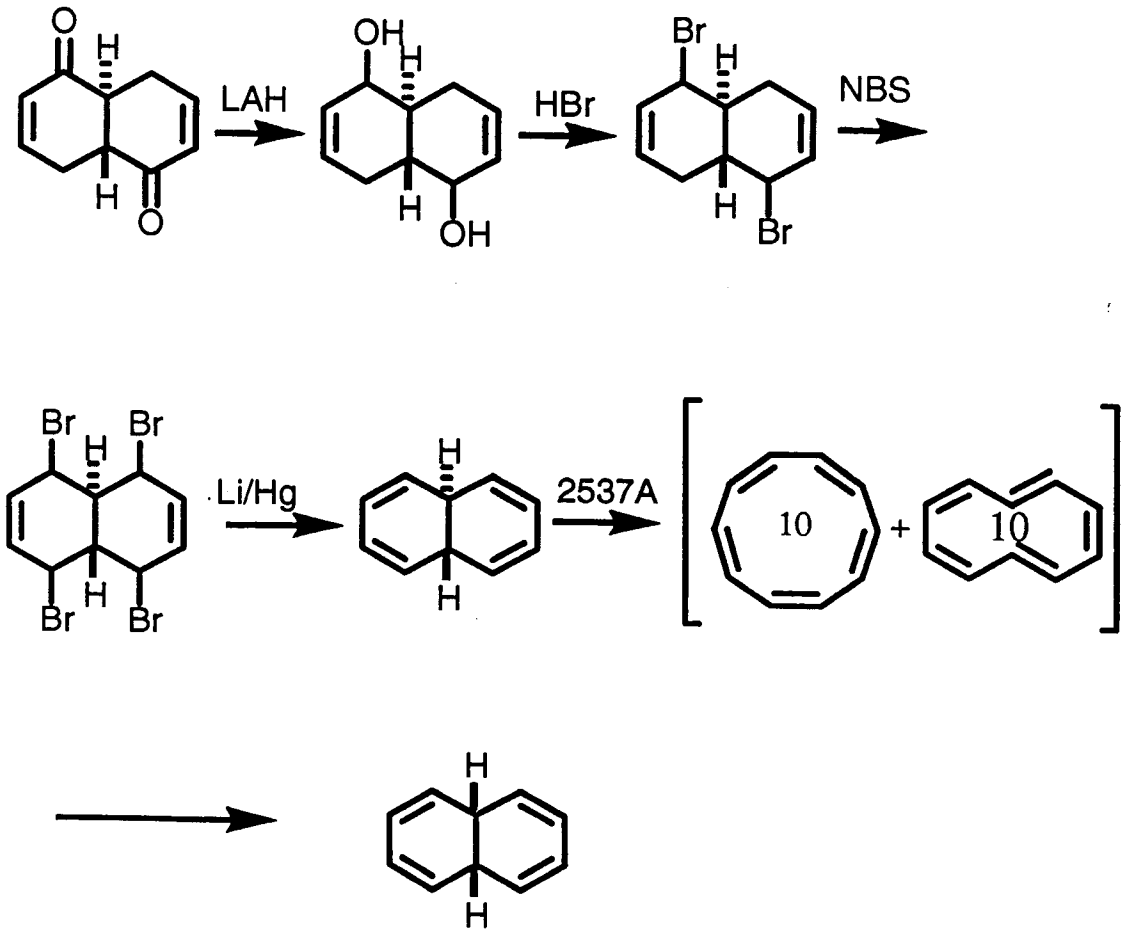
Figure 1. Structures of certain aromatic and pseudoaromatic compounds.



Hyp J. Dauben, Jr., James D. Wilson, and John L. Laity *JACS,* **1969,** *91, 1991*

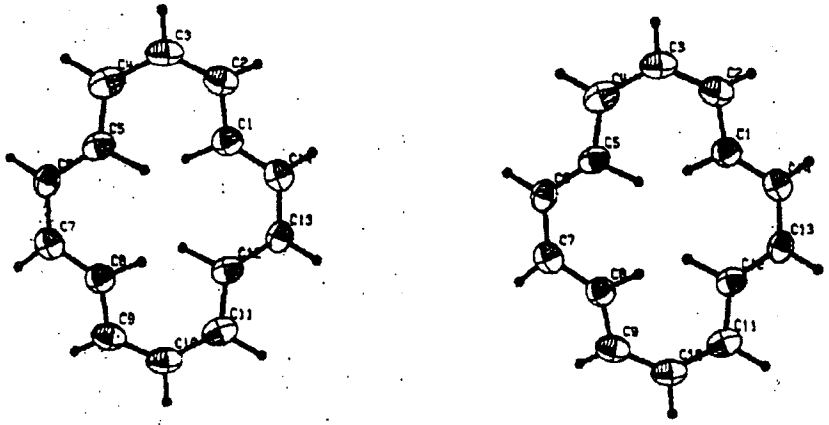
Landheer et.al. *TL,* **1975,** 349

Appendix C. Cyclodecapentaene



E.E. van Tamelen and T.L.Burloth *JACS,* **1967,** 89, 151

[14]-annulene X-RAY study



Stereoscopic view of a molecule of [14]annulene. The thermal ellipsoids are scaled to 25% probat

Planarity:+/-0.21Å(C)
+/-0.79Å(H)
Bonds vary,
No real alteration

Chian C. Chiang, Iain C. Paul*
W. A. Noyes Chemical Laboratory, University of Illinois
Urbana, Illinois 61801
Received Feb 28, 1972

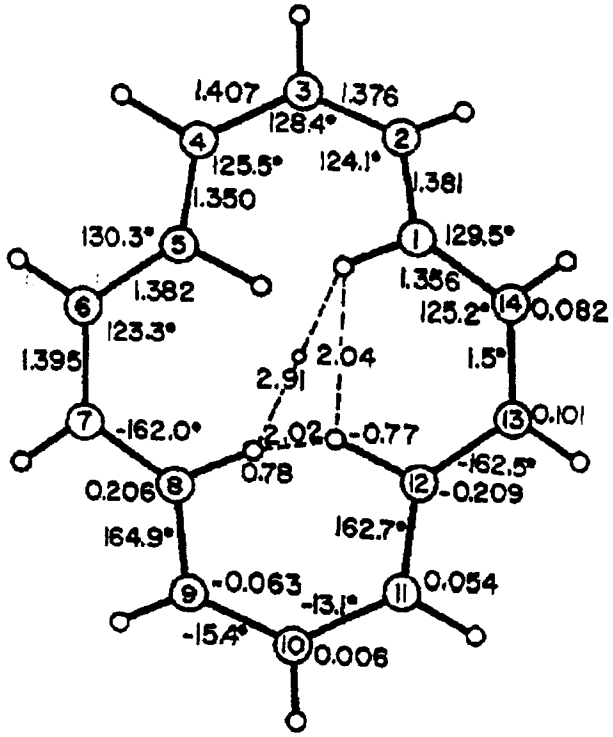


Figure 2. Molecular dimensions in [14]annulene. The upper half of the drawing shows the bond lengths (angströms) and bond angles (degrees). The lower part of the drawing (related by a center of inversion) shows the deviations of atoms (angströms) from the best plane through the carbon atoms, and the torsion angles around the C–C bonds (degrees). The esd's of the C–C bonds are 0.010 Å and of the C–C–C angles are 0.5°. According to the formula given by P. J. Huber in the appendix in E. Huber-Buser and J. D. Dunitz, *Helv. Chim. Acta*, **44**, 2027 (1961), the esd's of the torsion angles are approximately twice those of the valency angles.

I.C.Paul, C.C.Chiang *JACS*, **1972**, *94*, 4741

[16]-annulene X-RAY study

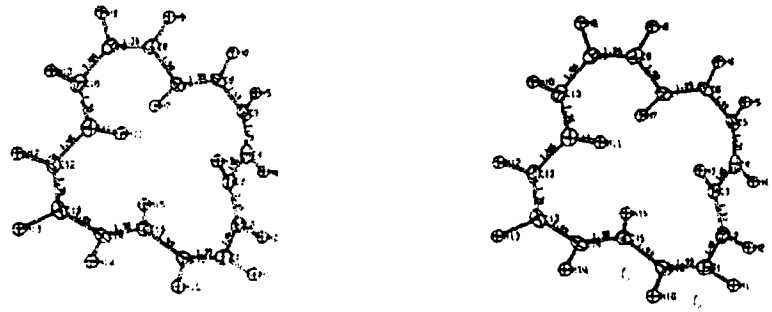


Figure 1. Stereoscopic view of the [16] annulene molecule looking along the *b* axis. Bond distances in Ångströms; standard deviation of C–C bond distances lie in range 0.010–0.015 Å.

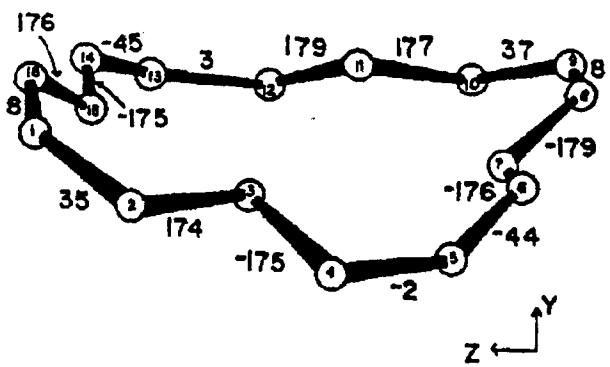


Figure 2. View of the [16]annulene molecule looking along the *a* axis. The dihedral angles along the bonds in the ring are given in degrees. The angle is taken as positive if, when viewed along the bond, the nearer substituent has to be rotated clockwise to eclipse the more distant substituent.

Average C-C=1.46A
Average C=C=1.34A

I.C.Paul, et.al *JACS*, **1968**, *90*, 6555