8

Aromaticity

Introduction

The meaning of the word *aromaticity* has evolved as understanding of the special properties of benzene and other aromatic molecules has deepened.[1] Originally, aromaticity was associated with a specific chemical reactivity. The aromatic hydrocarbons undergo substitution reactions in preference to addition. Later, the idea of special stability became more important. Benzene can be shown to be much lower in enthalpy than predicted by summation of the normal bond energies for the C=C, C−C, and C−H bonds in the Kekule representation of benzene (see p. 265). Aromaticity is now generally associated with this property of special stability of certain completely conjugated cyclic molecules. A major contribution to the stability of aromatic systems comes from the delocalization of π electrons in these molecules, which also imparts other properties that are characteristic of aromaticity, especially a diamagnetic ring current.

Aromaticity is usually described in MO terminology. Cyclic structures that have a particularly stable arrangement of occupied π molecular orbitals are called aromatic. *Hückel's rule*, a familiar expression of the relationship between an MO description of structure and aromaticity, is derived from Hückel molecular orbital (HMO) theory and states that *planar monocyclic completely conjugated hydrocarbons will be aromatic when the ring contains* $(4n+2)\pi$ *electrons*. HMO calculations assign the π-orbital energies of the cyclic unsaturated systems of ring size three to nine as shown in Figure 8.1. (See Section 1.5, p. 27 to review HMO theory.)

Orbitals below the dotted reference line in the figure are bonding orbitals; when they are filled, the molecule is stabilized. The orbitals that fall on the reference line are nonbonding; electrons in these orbitals are neither stabilizing nor destabilizing. The orbitals above the reference line are antibonding; electrons in these orbitals

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[1] M. Glukhovtsev, *J. Chem. Ed.*, **74**, 132 (1997); D. Lloyd, *J. Chem. Inf. Comput. Sci.*, **36**, 442 (1996), Z. Zhou, *Int. Rev. Phys. Chem.*, **11**, 243 (1992); J. P. Snyder, *Nonbenzenoid Aromatics*, Vol. 1, Academic Press, New York, 1969, Chap. 1. A series of reviews on many aspects of aromaticity is published in *Chem. Rev.*, **101**, 1115–1566 (2001).
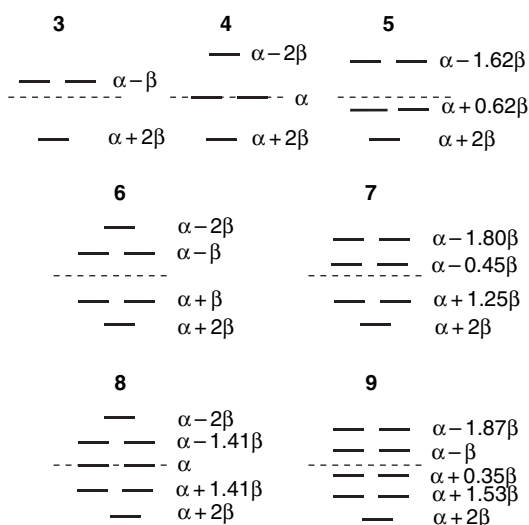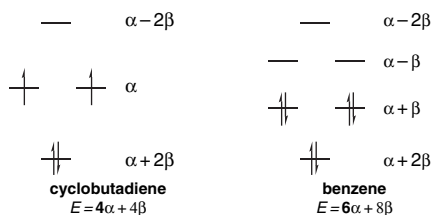
3

$\underline{\quad}\ \underline{\quad}\ \alpha-\beta$

$-----\ \alpha+2\beta$ (dashed)

$\underline{\quad}\quad \alpha+2\beta$

4

$\underline{\quad}\ \alpha-2\beta$

$----\ \underline{\quad}\ \underline{\quad}----\ \alpha$

$\underline{\quad}\ \alpha+2\beta$

5

$\underline{\quad}\ \underline{\quad}\ \alpha-1.62\beta$

$-------\ \bar{\alpha}+0.62\beta$

$\underline{\quad}\ \alpha+2\beta$

6

$\underline{\quad}\ \alpha-2\beta$

$\underline{\quad}\ \underline{\quad}\ \alpha-\beta$

$----------$

$\underline{\quad}\ \underline{\quad}\ \alpha+\beta$

$\underline{\quad}\ \alpha+2\beta$

7

$\underline{\quad}\ \underline{\quad}\ \alpha-1.80\beta$

$\underline{\quad}\ \underline{\quad}\ \alpha-0.45\beta$

$\underline{\quad}\ \underline{\quad}\ \alpha+1.25\beta$

$\underline{\quad}\ \alpha+2\beta$

8

$\underline{\quad}\ \alpha-2\beta$

$\underline{\quad}\ \underline{\quad}\ \alpha-1.41\beta$

$--\underline{\quad}-\underline{\quad}-\ \alpha$

$\underline{\quad}\ \underline{\quad}\ \alpha+1.41\beta$

$\underline{\quad}\ \alpha+2\beta$

9

$\underline{\quad}\ \underline{\quad}\ \alpha-1.87\beta$

$\underline{\quad}\ \underline{\quad}\ \alpha-\beta$

$----------\ \alpha+0.35\beta$

$\underline{\quad}\ \underline{\quad}\ \alpha+1.53\beta$

$\underline{\quad}\ \alpha+2\beta$

Fig. 8.1. HMO energies for conjugated planar ring systems of three to nine carbon atoms.

destabilize the molecule. The dramatic difference in properties of cyclobutadiene (extremely unstable) and benzene (very stable) are explicable in terms of these HMO diagrams.

cyclobutadiene
$E = 4\alpha + 4\beta$

$\underline{\quad}\ \alpha-2\beta$

$\uparrow\quad \uparrow\quad \alpha$

$\uparrow\downarrow\quad \alpha+2\beta$

benzene
$E = 6\alpha + 8\beta$

$\underline{\quad}\ \alpha-2\beta$

$\underline{\quad}\ \underline{\quad}\ \alpha-\beta$

$\uparrow\downarrow\quad \uparrow\downarrow\quad \alpha+\beta$

$\uparrow\downarrow\quad \alpha+2\beta$

Cyclobutadiene has two bonding electrons, but the other two electrons are unpaired because of the degeneracy of the two nonbonding orbitals. The two electrons in the nonbonding levels do not contribute to the stabilization of the molecule. The total HMO energy is $4\alpha + 4\beta$, which is the same as for two isolated double bonds. Furthermore, as these electrons occupy a high-energy orbital, they are particularly available for chemical reactions. As we shall see shortly, experimental evidence indicates that cyclobutadiene is rectangular rather than square. This modifies somewhat the orbital picture from the simple HMO pattern, which applies to a square geometry. The two nonbonding levels are no longer degenerate, so cyclobutadiene is not predicted to have unpaired electrons. Nevertheless, higher-level calculations agree with the Hückel concept in predicting cyclobutadiene to be an extremely unstable molecule with a high-lying HOMO. We will see that several methods of analysis indicate that cyclobutadiene is not only highly reactive, but is also *less stable* than an isolated diene. Cyclobutadiene is called *antiaromatic.*[2]

Simple Hückel calculations on benzene, in contrast, place all the π electrons in bonding MOs. The π-electron energy of the benzene molecule is calculated by

[2.] R. Breslow, *Acc. Chem. Res.*, **6**, 393 (1973).

summing the energies of the six π-electrons, which is $6\alpha + 8\beta$, lower by 2β than the value of $6\alpha + 6\beta$ for three isolated double bonds. Thus the HMO method predicts a special stabilization for benzene.

The eight-electron cyclic conjugated polyene is 1,3,5,7-cyclooctatetraene, which was first synthesized in 1911.[3] Cyclooctatetraene is not much different in reactivity and stability from noncyclic conjugated polyenes. It has no aromatic characteristics. Structural studies determined that cyclooctatetraene is nonplanar, and its most stable structure is tub-shaped. This reduces the overlap between the π bonds, and since the molecule is not planar, the HMO orbital pattern does not apply. Cyclooctatetraene is neither aromatic nor antiaromatic.

The pattern for planar conjugated systems established for cyclobutadiene, benzene, and cyclooctatetraene persists for larger rings. All $4n + 2$ systems are predicted to have all electrons paired in bonding MOs with net stabilization relative to isolated double bonds. In contrast, planar systems containing $4n$ π electrons are predicted to have two degenerate orbitals, each with one unpaired electron. This pattern is the theoretical basis of the Hückel rule.

8.1. Criteria of Aromaticity

HMO theory and Hückel's rule make a good starting point for considering the two molecules, benzene and cyclobutadiene, that are at opposite extremes of aromaticity. There are many other structures that can be described as aromatic or antiaromatic. In this section, we discuss various criteria of aromaticity and its effect on the properties of a few prototypical compounds. In the sections that follow, we look at various specific compounds, including charged rings and homoaromatic systems, as well as polycyclic and heterocyclic rings. We apply these criteria to evaluating aromaticity. We consider three types of criteria: (1) *energy data* indicating thermodynamic stabilization or destabilization; (2) *structural information*, particularly as it relates to bond lengths indicating delocalized structures; and (3) *electronic properties*, including energy levels, electron distribution, and polarizability. The third group of properties includes the response of the electrons to a magnetic field, which can be observed through NMR and magnetic susceptibility measurements. For the most part we use benzene, naphthalene, anthracene, and phenanthrene as examples of aromatic molecules, cyclobutadiene as an example of an antiaromatic molecule, and 1,3,5,7-cyclooctatetraene as a nonaromatic molecule.

8.1.1. The Energy Criterion for Aromaticity

One approach to evaluation of the aromaticity of a molecule is to determine the extent of thermodynamic stabilization. Attempts to describe stabilization of a given aromatic molecule in terms of simple HMO calculations have centered on the *delocalization energy*. The total π-electron energy of a molecule is expressed in terms of the energy parameters α and β that are used in HMO calculations. This energy value can be compared to that for a hypothetical localized version of the same molecule. The HMO energy for the π electrons of benzene is $6\alpha + 8\beta$. The same quantity for

[3.] R Willstatter and E. Waser, *Ber.*, **44**, 3423 (1911); R. Willstatter and M. Heidelberger, *Ber.*, **46**, 517 (1913); A. C. Cope and C. G. Overberger, *J. Am. Chem. Soc.*, **70**, 1433 (1948).

the hypothetical localized model cyclohexatriene is $6\alpha + 6\beta$, the sum of three isolated C=C bonds. The difference of 2β is called the *delocalization energy* or *resonance energy*. Although this quantity can be used for comparing related systems, it is not a measurable physical quantity; rather, it is a comparison between a real molecule and a hypothetical one and depends on the definition of the reference point.

There have been two general approaches to determining the amount of stabilization that results from aromatic delocalization. One is to use experimental thermodynamic measurements. Bond energies, as we discussed in Chapter 3, are nearly additive when there are no special interactions among the various bond types. Thus it is possible to assign such quantities as the heat of combustion or heat of hydrogenation of "cyclohexatriene" by assuming that it is a compound with no inter-action between the conjugated double bonds. For example, a very simple calculation of the heat of hydrogenation for cyclohexatriene would be to multiply the heat of hydrogenation of cyclohexene by 3, i.e., $3 \times 28.6 = 85.8 \, \text{kcal/mol}$. The actual heat of hydrogenation of benzene is 49.8 kcal/mol, suggesting a total stabilization or delocalization energy of 36 kcal/mol. The difference between the calculated and corresponding measured thermodynamic property of benzene is taken to be the aromatic stabilization. There are other, more elaborate, ways of approximating the thermodynamic properties of the hypothetical cyclohexatriene. There are also other possible reference points. Most estimates of the thermodynamic stabilization of benzene are in the range 20–40 kcal/mol, but the stabilization cannot be determined in an absolute sense since it depends on the choice of the reference molecules and the properties ascribed to them.

The second general approach to estimating aromatic stabilization is to use computational methods. This has already been illustrated by the discussion of benzene according to HMO theory, which assigns the stabilization energy as 2β units. More advanced MO and DFT methods can assign the stabilization energy in a more quantitative way. The most successful method is to perform calculations on the aromatic compound and on a linear, conjugated polyene containing the same number of double bonds.[4] This method assigns a resonance stabilization of zero to the polyene, even though it is known by thermodynamic criteria that conjugated polyenes do have some stabilization relative to isomeric compounds with isolated double bonds. In effect, this method defines the stabilization *over and above that present in the conjugated polyene*. With this definition, semiempirical MO calculations assign a value of about 20 kcal/mol to the resonance energy of benzene, relative to 1,3,5-hexatriene. The use of polyenes as reference compounds gives better agreement with experimental trends in stability than comparison with the sums of isolated double bonds. It is very significant that MO calculations indicate a *destabilization* of certain conjugated cyclic polyenes, cyclobutadiene in particular. This conclusion has recently been supported experimentally. The technique of photoacoustic calorimetry provided the first experimental thermodynamic data on cyclobutadiene. The ΔH_f value of $114 \pm 11 \, \text{kcal/mol}$ leads to a total destabilization of 87 kcal/mol, of which 32 kcal/mol is attributed to ring strain and 55 kcal/mol to antiaromaticity.[5]

The isodesmic reaction method (see Section 1.2.6) has also been applied to the calculation of the resonance stabilization of benzene. *Homodesmotic reactions*, a special version of isodesmic reactions, can also be used.[6] Homodesmotic reactions

4. M. J. S. Dewar and C. de Llano, *J. Am. Chem. Soc.*, **91**, 789 (1969).
5. A. A. Deniz, K. S. Peters, and G. J. Snyder, *Science*, **286**, 1119 (1999).
6. P. George, M. Trachtman, C. W. Bock, and A. M. Brett, *J. Chem. Soc., Perkin Trans. 2*, 1222 (1976); P. George, M. Trachtman, C. W. Bock, and A. M. Brett, *Tetrahedron*, **32**, 1357 (1976).

not only balance the bond types, but also match the hybridization of all atoms on both sides of the equation. For example, the stabilization of benzene, relative to 1,3-butadiene, can be calculated by the reaction below, which has 12 sp^2 carbons on each side of the equation.

$$\bigcirc \quad + \quad 3 \quad CH_2{=}CH_2 \quad \longrightarrow \quad 3 \quad CH_2{=}CH{-}CH{=}CH_2$$
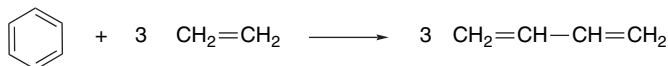
Isodesmic and homodesmotic reactions can use either experimental thermo-chemical data or energies obtained by MO or DFT calculations. There have been many specific reaction schemes and computational methods applied to calculation of stabilization energies.[7] With the above homodesmotic sequence, calculations at the MP4(SDTQ)/6-31G(d,p) level give the following stabilization (ΔE) values.[8]

	ΔE	$\Delta E/\pi$ Electron
Cyclobutadiene	-75.1	-18.8
Benzene	25.3	4.3
Cyclooctatetraene(planar)	-28.3	-3.6

The destabilization of cyclobutadiene is estimated to include 33.5 kcal/mol of strain. Planar cyclooctatetraene would also have some strain resulting from expansion of the bond angles. Because the calculations are referenced to butadiene, the stabi-lization is in addition to the stabilization of butadiene by conjugation. If the stabilization energy of butadiene is assigned as zero, the above reaction gives the resonance energy of benzene as 25.3 kcal/mol. If butadiene is considered to have a delocalization energy of 4.5 kcal/mol (see Section 3.1.2.3), the benzene stabilization energy is 29.8 kcal/mol. B3LYP/6-311+G** calculations on the same homodesmotic reaction led to a stabi-lization energy of 29.3 kcal/mol.[9]

This particular calculation may *underestimate* the relative stabilization, since it uses *trans*-1,3-butadiene as the model, rather than the *cis* geometry that is incorpo-rated into cyclic structures.[10] For example, the homodesmotic reaction below gives a stabilization energy of 30.5 kcal/mol *relative to cyclohexadiene*.[11] A feature of this scheme is that it incorporates many of the structural features of the system, such as ring strain, into both sides of the equation so that they should largely cancel. The net stabilization has been called the *aromatic stabilization energy*.

$$3 \quad \bigcirc \quad + \quad \bigcirc \quad \longrightarrow \quad \bigcirc \quad + \quad 3 \quad \bigcirc$$
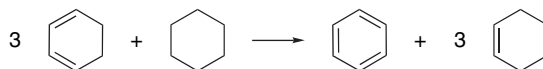
Another refinement of the isodesmic approach to defining aromatic stabi-lization is to compare methyl-substituted aromatics with the corresponding

[7] A. Skanke, R. Hosmane, and J. F. Liebman, *Acta Chem. Scand.*, **52**, 967 (1998).

[8] M. N. Glukhovtsev, R. D. Bach, and S. Laiter, *Theochem*, **417**, 123 (1997).

[9] P. v. R. Schleyer, H. Jiao, N. J. R. van Eikema Hommes, V. G. Malkin, and O. L. Malkina, *J. Am. Chem. Soc.*, **119**, 12669 (1997).

[10] M. K. Cyranksi, P. v. R. Schleyer, T. M. Krygowski, H. Jiao, and G. Hohlneicher, *Tetrahedron*, **59**, 1657 (2003).

[11] P. v. R. Schleyer, M. Manoharan, H. Jiao, and F. Stahl, *Org. Lett.*, **3**, 3643 (2001).

exo-methylene polyene analogs. For example, toluene can be compared with 5-methylene-1,3-cyclohexadiene. This reaction gives a stabilization of 33.2 kcal/mol using B3LYP/6-311+G** calculations.[12]

This sequence is not a suitable one for using experimental data, since the *exo*-methylene analogs are seldom available, but it is practical for computational approaches.

Although the stabilization of aromatic compounds is frequently associated with the delocalization of the π electrons, it is important to recognize that there are other large energy contributions to the difference between localized and delocalized structures, because the *nuclear positions are also different*. The method of separation of nuclear-nuclear, electron-electron, and nuclear-electron forces (see Topic 1.1) has been applied to cyclobutadiene and benzene.[13] According to this analysis, nuclear-nuclear interactions are destabilizing in both cyclobutadiene and benzene. Electron-electron forces are also destabilizing in benzene, but a very favorable nuclear-electron interaction is responsible for the net stabilization.

Net Stabilization of Delocalized Structure Relative to Localized Model

	Cyclobutadiene	Benzene
V_{ee}	+16.4	−84.4
V_{nn}	−43.4	−78.7
V_{ne}	−1.7	+168.7

These various approaches for comparing the thermodynamic stability of aromatic compounds with reference compounds all indicate that there is a large stabilization of benzene and an even greater destabilization of cyclobutadiene. These compounds are the best examples of aromaticity and antiaromaticity, and in subsequent discussions of other systems we compare their stabilization or destabilization to that of benzene and cyclobutadiene.

8.1.2. Structural Criteria for Aromaticity

Benzene is a perfectly hexagonal molecule with a bond length (1.39 Å) that is intermediate between single and double bonds between sp^2 carbons. Cyclobutadiene, on the other hand, adopts a rectangular shape. This contrasting behavior suggests that *bond length alternation* might be a useful criterion for assessing aromaticity, and several such schemes have been developed. One such system, called HOMA (for harmonic oscillator model for aromaticity), developed by Krygowski and co-workers,[14] takes

12. P. v. R. Schleyer and F. Puhlhofer, *Org. Lett.*, **4**, 2873 (2002).
13. Z. B. Maksic, D. Baric, and I. Petanjek, *J. Phys. Chem. A*, **104**, 10873 (2000).
14. J. Kruszewski and T. M. Krygowski, *Tetrahedron Lett.*, 3839 (1972).

both bond length alternation and bond stretching into consideration. The aromaticity index HOMA is formulated as

$$\text{HOMA} = 1 - [\alpha(R_{\text{opt}} - R_{\text{av}})^2 + \frac{\alpha}{n}\Sigma(R_{\text{av}} - R_{\text{i}})^2] \tag{8.1}$$

where R_{av} is average bond length, R_{opt} is the optimum bond length, R_{i} is an individual bond length, n is the number of bonds, and α is a constant such that HOMA is equal to zero for a single localized structure. The HOMA equation can be rewritten as

$$\text{HOMA} = 1 - \frac{\alpha}{n}\sum\left[R_{\text{opt}} - R_i\right]^2 \tag{8.2}$$

The R_{opt} values are derived from butadiene, which is thereby the implicit standard of the definition. For C−C bonds, $\alpha = 257.7\,\text{Å}^{-2}$ and $R_{\text{opt}} = 1.388\,\text{Å}$. Further definition of bond lengths is required for structures with heteroatoms.

In the formulation in Equation (8.1), the first term, the deviation from the optimum length, accounts for the energy associated with bond length effects, and the second term, which reflects deviation from the average, accounts for bond alternation. The HOMA energy and alternation terms have been calculated for many aromatic compounds.[15] The values for benzene, naphthalene, anthracene, and phenanthrene are shown below.[16] Note the decrease as the molecules get larger. HOMA indices can also be assigned to the individual rings in polycyclic structures. A relatively low HOMA is assigned to the center ring in phenanthrene. We will see later that this is in accord with other properties of phenanthrene. In contrast, the center ring in anthracene has a slightly higher index than the terminal rings.
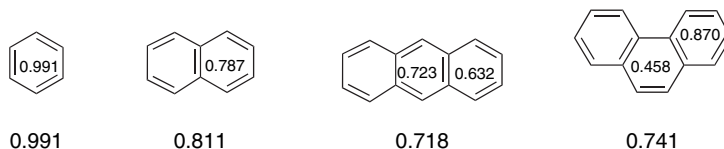
Another aromaticity index based on bond lengths was devised by Bird.[17] The input into the index are bond order values derived from bond lengths. (See Section 1.4.6 to review the relationship between bond length and bond order.) The formulation of the index is

$$I = 100(1 - \frac{V}{V_k})V = \frac{100}{\overline{N}}\sqrt{\frac{\sum(N - \overline{N})^2}{n}} \text{ and } N = \frac{a}{R_2} - b \tag{8.3}$$

where $\overline{N}$ is the arithmetic mean of bond orders. V_k is the value of V for the corresponding localized structures, and a and b are constants for each bond type.

The index I_A is assigned as 100 for benzene. The values are scaled for ring size and ring fusions, and increase with ring size so that naphthalene (142) and anthracene (206) have higher indices than benzene. This method is particularly useful for comparing heterocyclic compounds with hydrocarbons (see Section 8.6).

[15.] T. M. Krygowski and M. Cyranski, *Tetrahedron*, **52**, 1713 (1996).
[16.] M. K. Cyranski, B. T. Stepien, and T. M. Krygowski, *Tetrahedron*, **56**, 9663 (2000).
[17.] C. W. Bird, *Tetrahedron*, **41**, 1409 (1985); C. W. Bird, *Tetrahedron*, **48**, 335 (1992); C. W. Bird, *Tetrahedron*, **52**, 9945 (1996); C. W. Bird, *Tetrahedron*, **54**, 4641 (1998).

8.1.3. Electronic Criteria for Aromaticity

As discussed in the Introduction, Hückel's rule is an electronic criterion for aromaticity, and is based on the configuration of the π electrons. Another characteristic of aromatic compounds is a relatively large HOMO-LUMO gap, which indicates the absence of high-energy, reactive electrons, in agreement with the reduced reactivity of aromatic compounds to electrophilic reagents. This facet of electronic configuration can be expressed in terms of hardness (see p. 96 for the definition of hardness in terms of DFT theory).[18]

$$\eta = (\varepsilon_{HOMO} - \varepsilon_{LUMO})/2$$

The numerical value of hardness obtained by HMO calculations correlates with the stability of aromatic compounds.[19] The energy gap can also be compared with polyene reference molecules to give "relative hardness." By this measure, the relative hardness of benzene is 0.765β when butadiene is assigned as 0. MNDO calculations have also been used in this context.[20]

The correlation can be given an experimental basis when hardness is related to molar refractivity[21]:

$$\eta = \frac{19.6}{(R_D)^3} \tag{8.4}$$

Molar refractivity is easily derived from the refractive index. Hardness measured in this way correlates with other aromaticity criteria such as resonance energy per electron for a variety of hydrocarbons and heterocyclic molecules (see p. 747).[22]

An experimental measure of the HOMO-LUMO gap is the reduction and oxidation potential of the ring.[23] A range of benzenoid and nonbenzenoid reduction potentials correlates with the LUMO energy, as calculated by a modified HMO method.[24]

NMR spectroscopy also provides an experimental tool capable of assessing aromaticity. Aromatic compounds exhibit a *diamagnetic ring current*. Qualitatively, this ring current can be viewed as the result of migration of the delocalized π electrons under the influence of the magnetic field in an NMR spectrometer. The ring current results in a large magnetic anisotropy in aromatic compounds. The induced ring current gives rise to a local magnetic field that is opposed to the direction of the applied magnetic field. Nuclei in a region above or below the plane of an aromatic ring are shielded by the induced field and appear at relatively high field in the NMR spectrum, whereas nuclei in the plane of the ring—i.e., the atoms bound directly to the ring—occur at downfield positions. Antiaromatic compounds have a *paramagnetic ring current* and show opposite effects. These chemical shifts are evidence of *magnetic anisotropy*.[25] The detailed analysis of ^1H and ^{13}C chemical shifts is complicated.

[18.] F. De Proft and P. Geerlings, *Chem. Rev.*, **101**, 1451 (2001).

[19.] Z. Zhou and R. G. Parr, *J. Am. Chem. Soc.*, **111**, 7371 (1989).

[20.] Z. Zhou and H. V. Navangul, *J. Phys. Org. Chem.*, **3**, 784 (1990); Z. Zhou, *Int. Rev. Phys. Chem.*, **11**, 243 (1992).

[21.] L. Komorowski, *Structure and Bonding*, **80**, 45 (1993).

[22.] C. W. Bird, *Tetrahedron*, **53**, 3319 (1997).

[23.] A. J. Fry and P. C. Fox, *Tetrahedron*, **42**, 5255 (1986).

[24.] A. Streitwieser, *J. Am. Chem. Soc.*, **82**, 4123 (1960).

[25.] R. C. Haddon, *J. Am. Chem. Soc.*, **101**, 1722 (1979); J. Aihara, *J. Am. Chem. Soc.*, **103**, 5704 (1981); R. C. Haddon and K. Raghavachari, *J. Am. Chem. Soc.*, **107**, 289 (1985); S. Kuwajima and Z. G. Soos, *J. Am. Chem. Soc.*, **109**, 107 (1987).

The ^1H and ^{13}C shifts are also strongly dependent on carbon hybridization. In aromatic compounds, the ring current makes a significant contribution to the overall chemical shift, but does not appear to be the dominant factor.[26] Figure 8.2 is a representation of the shielding and deshielding areas of the benzene ring.

The relationship between chemical shift phenomena and aromaticity can be put on a numerical basis by calculation of the magnetic field at the center of the ring. These values, called the *nucleus independent chemical shift* (NICS), show good correlation with other manifestations of aromaticity.[27] Benzenoid hydrocarbons such as benzene, naphthalene, and anthracene show values of about -9 to -10 ppm. Heteroaromatic five-membered rings show somewhat more negative values (pyrrole, -15.1; thiophene, -13.6; furan, -12.3). Aromatic ions such as cyclopentadienide (-14.3) and cycloheptatrienylium (-7.6) are also negative. Antiaromatic species, including cyclobutadiene ($+27.6$) and borole ($+17.5$) are positive. Saturated compounds such as cyclohexane have values near zero. It is also possible to calculate NICS values for individual rings in a polycyclic system. The NICS value can be affected by other structural features that are not directly related to the aromatic ring current. The maximum for the ring current is located somewhat above the ring and other factors are reduced at this location, so that calculation of the NICS 1.0 Å above and below the ring is useful.[28]

Several other methods have been devised to analyze the ring current effect. One approach is to isolate the individual orbitals that have π character and use them for the NICS computation.[29] Another quantity that relates anisotropic shielding to aromaticity is called the ARCS, *aromatic ring current shielding*.[30] As with NICS, it is computed
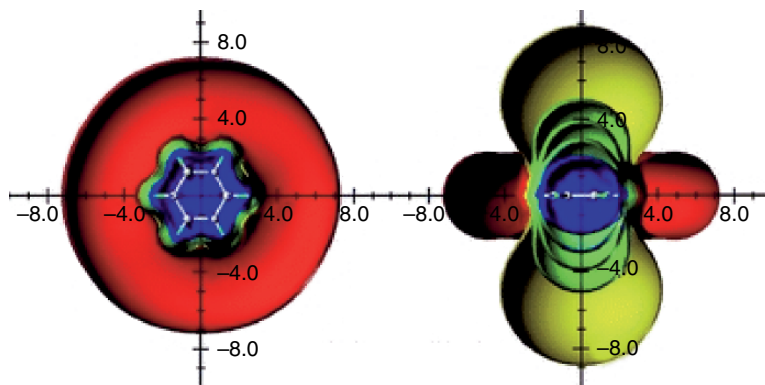
Fig. 8.2. Areas of shielding and deshielding in and perpendicular to the plane of the benzene ring. Reproduced from *J. Chem. Soc., Perkin Trans. 2*, 1893 (2001), by permission of the Royal Society of Chemistry. (See also color insert.)

[26.] U. Fleischer, W. Kutzelnigg, P. Lazzeretti, and V. Muehlenkamp, *J. Am. Chem. Soc.*, **116**, 5298 (1994); S. Klod and E. Kleinpeter, *J. Chem. Soc., Perkin Trans. 2*, 1893 (2001); C. S. Wannere and P. v. R. Schleyer, *Org. Lett.*, **5**, 605 (2003).

[27.] P. v. R. Schleyer, C. Maerker, A. Dransfeld, H. Jiao, and N. J. P. van Eikema Hommes, *J. Am. Chem. Soc.*, **118**, 6317 (1996).

[28.] P. v. R. Schleyer, H. Jiao, N. J. R. van Eikema Hommes, V. G. Malkin, and O. L. Malkina, *J. Am. Chem. Soc.*, **119**, 12669 (1997); P. v. R. Schleyer, M. Manoharan, Z. -X. Wang, B. Kiran, H. Jiao, R. Puchta, and N. J.R. van Eikema Hommes, *Org. Lett.*, **3**, 2465 (2001).

[29.] C. Corminboeuf, T. Heine, and J. Weber, *Phys. Chem. Chem. Phys.*, **5**, 246 (2003).

[30.] J. Juselius and D. Sundholm, *Phys. Chem. Chem. Phys.*, **1**, 3429 (1999).

theoretically and defined in such a way that it can be used to compare different rings. The units are nanoamperes (nA), and the calculated ring currents are found to increase in more electron-rich systems, as is the case with NICS. Whereas benzene is 32 nA, pyrrole is 41.4 nA and cyclopentadienide is 72.2 nA. Conversely, it is lower for the cycloheptatrienyl cation (26.1 nA); thiophene (32.1 nA) is very similar to benzene; and nonaromatic compounds such as cyclohexane or 1,4-cyclohexadiene have much smaller values (2.1 and 1.7 nA, respectively).

Another electronic property associated with aromaticity is *magnetic susceptibility*, which is determined by measuring the force exerted on the sample by a magnetic field.[31] Magnetic susceptibility is closely related to polarizability and is different in the plane and perpendicular to the plane of the ring. It can be determined by various spectroscopic measurements,[32] as well as by using an NMR spectrometer.[33] It is observed that aromatic compounds have enhanced magnetic susceptibility, called *exaltation* (Λ), relative to values predicted on the basis of the localized structural components.[34]

Magnetic Susceptibility Exaltation for Some Aromatic Hydrocarbons

Compound	Λ
Benzene	13.7
Naphthalene	30.5
Anthracene	48.6
Phenanthrene	46.2
Azulene	29.6

Magnetic susceptibility can also be calculated by computational methods; calculation by the B3LYP method correctly reproduces some of the trends in stability among the benzo[b]- and benzo[c]- derivatives of five-membered heterocycles.[35] The benzenoid benzo[b]- isomers are much more stable compounds than the quinoid benzo[c] isomers.

55.7	53.9	51.9	51.3	49.6	46.8
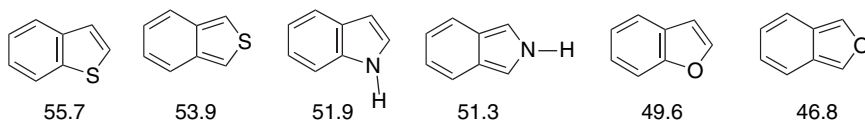
Because all of these electronic aspects of aromaticity are ultimately derived from the electron distribution, we might ask whether representations of electron density reveal any special features in aromatic compounds. The electron density of the π electrons can be mapped through the MESP (molecular electrostatic potential, see Section 1.4.5).[36] The MESP perpendicular to the ring is completely symmetrical for benzene, as would be expected for a delocalized structure and is maximal at about

31. E. A. Boudreaux and R. R. Gupta, in *Physical Methods in Heterocyclic Chemistry*, R. R. Gupta, ed., Wiley-Interscience, New York, 1984, pp. 281–311.
32. W. H. Flygare, *Chem. Rev.*, **74**, 653 (1974).
33. K. Frei and H. J. Bernstein, *J. Chem. Phys.*, **37**, 1891 (1962).
34. H. J. Dauben, J. D. Wilson, and J. L. Laity, *J. Am. Chem. Soc.*, **90**, 811 (1968); P. v. R. Schleyer and H. Jiao, *Pure Appl. Chem.*, **68**, 209 (1996); P. Friedman and K. F. Ferris, *Int. J. Quantum Chem.*, **24**, 843 (1990).
35. B. S. Jursic, *J. Heterocycl. Chem.*, **33**, 1079 (1996).
36. C. H. Suresh and S. R. Gadre, *J. Org. Chem.*, **64**, 2505 (1999).

1.73 Å above and below the ring. In naphthalene, there are different values for the different bond types and also shifts in the position of the maxima. The 1,2-bonds, which have higher double-bond character, have more negative MESP than the 2,3-, 8a-1, or 4a,8a-bonds. The maximum in the MESP is also closer to the ring for these bonds. The trend continues for anthracene and is particularly accentuated for phenanthrene. The 9,10-bond in phenanthrene has the closest maxima with respect to the ring, which suggests considerable localization of the 9,10-bond in phenanthrene.
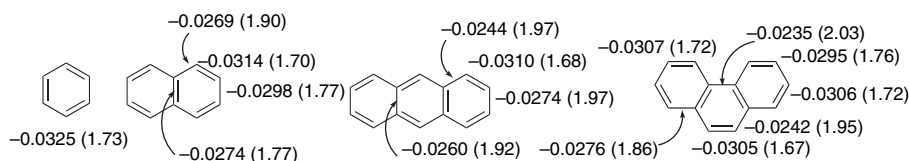
Value of MESP and distance of maxima.

These data are consistent with both the bond order concept (see p. 76) and the idea that benzenoid structures are preferred to quinoid structures (see p. 724).

Atoms in molecules (AIM) concepts have also been applied to analysis of electron density distribution in benzene and several polycyclic hydrocarbons.[37] (See Section 1.4.3 to review AIM electron density indicators.) A correlation was found between the charge density at the bond critical point and bond lengths. Shorter bonds had higher ρ_c and more negative $-L(\nabla^2\rho_c)$, which is also true for other types of bonds. The shorter bonds also have greater ellipticity. Matta and Hernandez-Trujillo found that bond lengths were related to ρ_c for a series of aromatic molecules[38] They determined the delocalization indices, which indicate the number of electrons shared by adjacent atoms, for a number of rings. These values are 0.99, 1.39, and 1.89, respectively, for ethane, benzene, and ethene, the numbers reflecting the additional electron density associated with the multiple bonds. These values were also calculated for several fused-ring systems, as shown below. The bond ellipticity was also calculated and is given with the structures (italic numbers). Bond ellipticity increases with bond order, reflecting the accumulation of π-electron density.
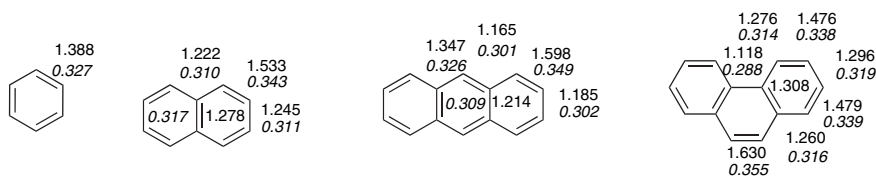
These values faithfully capture both structural and reactivity variations among the ring systems. The highest bond orders are found at the 1,2-bond of naphthalene and in anthracene. For phenanthrene, the highest bond order is between the 9,10 positions in the center ring. There is substantially less bond alteration around the periphery of phenanthrene than in anthracene. A pictorial representation of this information is given in Figure 8.3. The overall molecular shape is represented by the 0.001 au isodensity

[37]. S. T. Howard and T. M. Krygowski, *Can. J. Chem.*, **75**, 1174 (1997).
[38]. C. F. Matta and J. Hernandez-Trujillo, *J. Phys. Chem. A*, **107**, 7496 (2003).
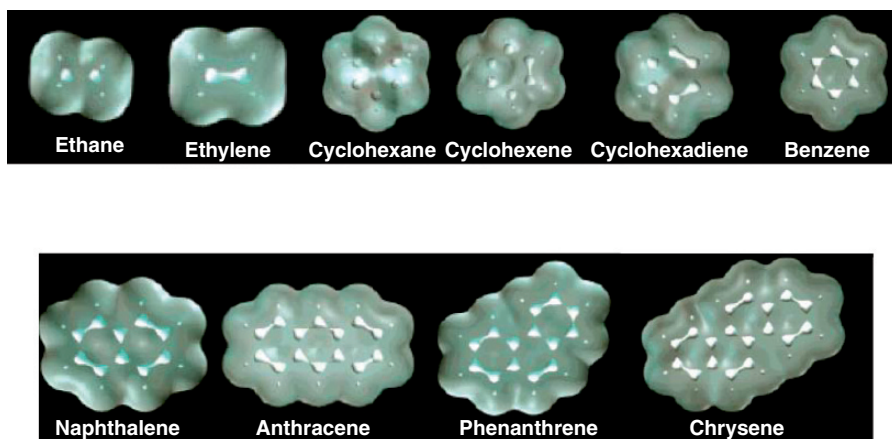
Fig. 8.3. Comparison of electron density as a function of bond order. See text for discussion. Reproduced from *J. Phys. Chem. A*, **107**, 7496 (2003), by permission of the American Chemical Society. (See also color insert.)

surface (gray). The inner lighter surface uses the 0.3274 au surface, which corresponds to the ρ_c for benzene. Bonds with higher ρ_c and higher bond order show merged density at this level. Bonds with lower ρ_c show separation of density at this level between the atoms.

The picture is also consistent with the intuitive idea that the best structure for any given polycyclic molecule is the one with the maximum number of benzene-like rings.[39] According to this concept the two rings in naphthalene are identical, but less aromatic than the benzene ring. The external rings in phenanthrene are more aromatic than the central ring, whereas the central ring is more aromatic in anthracene.
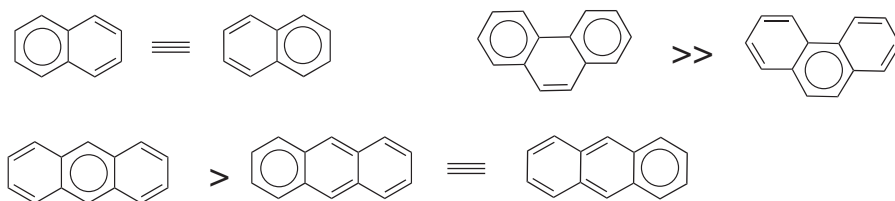
8.1.4. Relationship among the Energetic, Structural, and Electronic Criteria of Aromaticity

It has been argued that there are two fundamental aspects of aromaticity, one reflecting the structural and energetic facets and the other related to electron mobility.[40] Parameters of aromaticity such as bond length and stabilization energy appear to be largely separate from the electronic criteria, such as diamagnetic ring current. However, there is often a correlation between the two kinds of measurements. The

39. E. Clar, *The Aromatic Sextet*, John Wiley & Sons, London, 1972.
40. A. R. Katritzky, P. Barczynski, G. Musumarra, D. Pisano, and M. Szafran, *J. Am. Chem. Soc.*, **111**, 7 (1989); A. R. Katritzky, M. Karelson, S. Sild, T. M. Krygowski, and K. Jug, *J. Org. Chem.*, **63**, 5228 (1998); V. I. Minkin, M. N. Glukhovtsev, and B. Ya. Simkin, *Aromaticity and Antiaromaticity*, Wiley, New York, 1994.

more stabilized compounds exhibit the greatest magnetic susceptibility.[41] The various criteria all correlate, although there may be variation in the degree of correlation for different types of compounds.[42] Aromaticity is thus best conceived of as a single characteristic owing to structural factors that results in both stabilization and the phenomena associated with electron mobility.

8.2. The Annulenes

The term *annulene* refers to completely conjugated monocyclic polyenes.[43] The synthesis and study of annulenes has been extended well beyond the first several members of the series, cyclobutadiene, benzene, and cyclooctatetraene, which were described in the Introduction. The generality and limits of the Hückel rule can be tested by considering the properties of the annulene series. In this section, we consider the properties of the annulenes and related compounds in the context of aromaticity.

8.2.1. Cyclobutadiene

Although several derivatives of cyclobutadiene are known and are discussed shortly, cyclobutadiene itself has been observed only as a *matrix-isolated species*, that is trapped at very low temperature in a frozen inert gas. The first successful synthesis of cyclobutadiene was achieved by release from a stable iron complex.[44] Various trapping agents react with cyclobutadiene to give Diels-Alder adducts, indicating that it is reactive as both a diene and a dienophile.[45] Dehalogenation of *trans*-3, 4-dibromocyclobutene gave the same reaction products.[46]
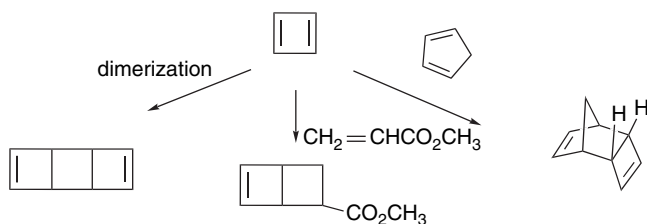
In the absence of trapping agents, a characteristic dimer is produced, which is the result of one cyclobutadiene molecule acting as a diene and the other as a dienophile in a Diels-Alder reaction. This dimerization is an extremely fast reaction and limits the lifetime of cyclobutadiene, except at extremely low temperatures.

41. P. v. R. Schleyer, P. K. Freeman, H. Jiao, and B. Goldfuss, *Angew. Chem. Int. Ed. Engl.*, **34**, 337 (1995); C. W. Bird, *Tetrahedron*, **52**, 9945 (1996).
42. M. K. Cyranski, T. M. Krygowski, A. R. Katritzky, and P. v. R. Schleyer, *J. Org. Chem.*, **67**, 1333 (2002).
43. F. Sondheimer, *Pure Appl. Chem.*, **28**, 331 (1971); *Acc. Chem. Res.*, **5**, 81 (1972).
44. L. Watts, J. D. Fitzpatrick, and R. Pettit, *J. Am. Chem. Soc.*, **87,** 3253 (1965).
45. L. Watts, J. D. Fitzpatrick, and R. Pettit, *J. Am. Chem. Soc.*, **88**, 623 (1966); J. C. Barborak, L. Watts, and R. Pettit, *J. Am. Chem. Soc.*, **88**, 1328 (1966); D. W. Whitman and B. K. Carpenter, *J. Am. Chem. Soc.*, **102**, 4272 (1980).
46. E. K. G. Schmidt, L. Brener, and R. Pettit, *J. Am. Chem. Soc.*, **92**, 3240 (1970).

Cyclobutadiene can also be prepared by photolysis of several different precursors at very low temperature in solid inert gases.[47] These methods provide cyclobutadiene in a form that is amenable for spectroscopic study. Analysis of the infrared spectrum of the product and deuterated analogs generated from labeled precursors have confirmed the theoretical conclusion that cyclobutadiene is a rectangular molecule.[48]

1.567 Å

1.346 Å
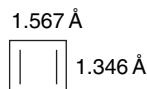
A number of alkyl-substituted cyclobutadienes have been prepared by related methods.[49] Increasing alkyl substitution enhances the stability of the compounds. The tetra-*t*-butyl derivative is stable up to at least 150°C, but is very reactive toward oxygen.[50] This reactivity reflects the high energy of the HOMO. The chemical behavior of the cyclobutadienes is in excellent accord with that expected from the theoretical picture of the structure of these compounds.

While simple HMO theory assumes a square geometry for cyclobutadiene, most MO methods predict a rectangular structure as the minimum-energy geometry.[51] The rectangular structure is calculated to be strongly destabilized (antiaromatic) with respect to a polyene model.[52] With HF/6-31G* calculations, for example, cyclobutadiene is found to have a negative resonance energy of –54.7 kcal/mol, relative to 1,3-butadiene. Furthermore, 30.7 kcal of strain is found, giving a total destabilization of 85.4 kcal/mol.[53] G2 and MP4/G-31(d,p) calculations arrive at an antiaromatic destabilization energy of about 42 kcal/mol.[54] A homodesmotic reaction incorporating polyradicals gives a value of 40.3 as the antiaromatic destabilization at the MP4(SDQ)/6-31G(d,p) level.[55] Recently, the technique of photoacoustic calorimetry provided the first experimental thermodynamic data on cyclobutadiene. The ΔH_f value of 114 ± 11 kcal/mol that was found leads to a total destabilization of 87 kcal/mol, of which 32 kcal/mol is attributed to ring strain and 55 kcal/mol to antiaromaticity.[56]

[47] G. Maier and M. Scheider, *Angew. Chem. Int. Ed. Engl.*, **10**, 809 (1971); O. L. Chapman, C. L. McIntosh, and J. Pancansky, *J. Am. Chem. Soc.*, **95**, 614 (1973); O. L. Chapman, D. De La Cruz, R. Roth, and J. Pancansky, *J. Am. Chem. Soc.*, **95**, 1337 (1973); C. Y. Lin and A. Krantz, *J. Chem. Soc., Chem. Commun.*, 1111 (1972); G. Maier, H. G. Hartan, and T. Sayrac, *Angew. Chem. Int. Ed. Engl.*, **15**, 226 (1976); H. W. Lage, H. P. Reisenauer, and G. Maier, *Tetrahedron Lett.*, **23**, 3893 (1982).

[48] S. Masamune, F. A. Souto-Bachiller, T. Machiguchi, and J. E. Bertie, *J. Am. Chem. Soc.*, **100**, 4889 (1978).

[49] G. Maier, *Angew. Chem. Int. Ed. Engl.*, **13**, 425 (1974); S. Masamune, *Tetrahedron*, **36**, 343 (1980).

[50] G. Maier, S. Pfriem, U. Schafer, and R. Matusch, *Angew. Chem. Int. Ed. Engl.*, **17**, 520 (1978).

[51] J. A. Jafri and M. D. Newton, *J. Am. Chem. Soc.*, **100**, 5012 (1978); W. T. Borden, E. R. Davidson, and P. Hart, *J. Am. Chem. Soc.*, **100**, 388 (1978); H. Kollmar and V. Staemmler, *J. Am. Chem. Soc.*, **99**, 3583 (1977); M. J. S. Dewar and A. Komornicki, *J. Am. Chem. Soc.*, **99**, 6174 (1977); B. A. Hess, Jr., P. Carsky, and L. J. Schaad, *J. Am. Chem. Soc.*, **105**, 695 (1983); H. Kollmar and V. Staemmler, *J. Am. Chem. Soc.*, **100**, 4304 (1978); C. van Wullen and W. Kutzelnigg, *Chem. Phys. Lett.*, **205**, 563 (1993).

[52] M. N. Glukhovtsev, S. Laiter, and A. Pross, *J. Phys. Chem.*, **99**, 6828 (1995).

[53] B. A. Hess, Jr., and L. J. Schaad, *J. Am. Chem. Soc.*, **105**, 7500 (1983).

[54] M. N. Glukhovtsev, R. D. Bach, and S. Laiter, *Theochem*, **417**, 123 (1997).

[55] C. H. Suresh and N. Koga, *J. Org. Chem.*, **67**, 1965 (2002).

[56] A. A. Deniz, K. S. Peters, and G. J. Snyder, *Science*, **286**, 1119 (1999).

8.2.2. Benzene

[6]Annulene is benzene. Its properties are so familiar to students of organic chemistry that not much need be said here. It is the parent compound of a vast series of derivatives. As we indicated in Section 8.2.1, benzene exhibits all the properties associated with aromaticity. It shows exceptional thermodynamic stability and its perfectly hexagonal structure sets the standard for bond uniformity. Benzene is much less reactive than conjugated polyenes toward electrophiles, which is in line with the energy of the HOMO of benzene being lower than that for the HOMO of a conjugated polyene. Benzene also exhibits NMR and magnetic susceptibility criteria consistent with aromaticity.

8.2.3. 1,3,5,7-Cyclooctatetraene

The next higher annulene, cyclooctatetraene, is nonaromatic.[57] It is readily isolable and the chemical reactivity is normal for a polyene. X-ray structure determination shows that the molecule is tub-shaped,[19] and therefore is not a planar system to which the Hückel rule applies. The bond lengths around the ring alternate as expected for a polyene. The C=C bonds are 1.33 Å, whereas the C−C bonds are 1.462 Å in length.[58] Thermodynamic analysis provides no evidence of any special stability.[59] There have been both experimental and theoretical studies aimed at estimating the relative stability of the planar form of cyclooctatetraene.[60] HF/6-31G* calculations find the completely delocalized D_{8h} structure to be about 4.1 kcal higher in energy than the conjugated planar D_{4h} structure, suggesting that delocalization leads to destabilization.[61] Similar results are obtained using MP2/CASSCF calculations.[62]

	D_{2d}	D_{4d}	D_{8d}
Relative Energy	0	10.6 kcal/mol	14.7 kcal/mol

These two energies are, respectively, comparable to the experimental activation energies for conformation inversion of the tub conformer and bond shifting, suggesting that the two planar structures might represent the transition states for those processes. The E_a have been measured for several substituted cyclooctatetraenes. According to

[57.] G. Schroeder, *Cyclooctatetraene*, Verlag Chemie, Weinheim, 1965; G. I. Fray and R. G. Saxton, *The Chemistry of Cyclooctatetraene and Its Derivatives*, Cambridge University Press, Cambridge, 1978.

[58.] M. Traetteberg, *Acta Chem. Scand.*, **20**, 1724 (1966).

[59.] R. B. Turner, B. J. Mallon, M. Tichy, W. v. E. Doering, W. Roth, and G. Schroeder, *J. Am. Chem. Soc.*, **95**, 8605 (1973).

[60.] L. A. Paquette, *Acc. Chem. Res.*, **26**, 57 (1993).

[61.] D. A. Hrovat and W. T. Borden, *J. Am. Chem. Soc.*, **114**, 5879 (1992); P. Politzer, J. S. Murray, and J. M. Seminario, *Int. J. Quantum Chem.*, **50**, 273 (1994).

[62.] J. L. Andres, D. Castano, A. Morreale, R. Palmeiro, and R. Gomperts, *J. Chem. Phys.*, **108**, 203 (1998).

these studies the ring inversion TS is usually about 2 kcal/mol below the bond shift TS.[60] This result implies a small destabilization of the delocalized structure.

ring inversion   bond shift
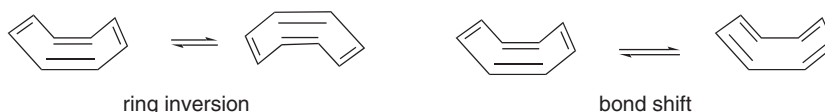
8.2.4. [10]Annulenes—1,3,5,7,9-Cyclodecapentaene Isomers

Larger annulenes permit the incorporation of *trans* double bonds into the rings, and isomeric structures are possible beginning with [10]annulene. According to the Hückel rule, [10]annulene would be aromatic if it were planar. However, all the 1,3,5,7,9-cyclodecapentaene isomers suffer serious steric strain that prevents the planar geometry from being adopted. The *Z,E,Z,Z,E*-isomer, which has minimal bond angle strain, suffers a severe nonbonded repulsion between the two internal hydrogens. The most stable structures are called the twist, boat, and heart.

twist   boat   heart

Z,E,Z,Z,E   *E,Z,Z,Z,Z–*   *Z,Z,Z,Z,Z–*   *E,Z,Z,Z,Z-*
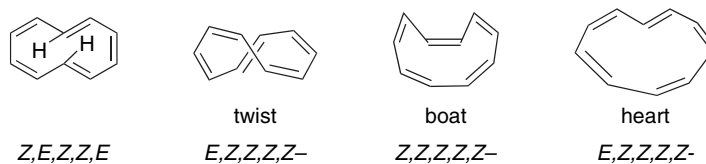
The *Z,Z,Z,Z,Z*-isomer is required by geometry to have bond angles of 144°C to maintain planarity and would therefore be destabilized by distortion of the normal trigonal bond angle. According to CCSD(T)/TZ2P-level calculations, the most stable structure is the twist form of the *E,Z,Z,Z,Z*-isomer.[63] This isomer also has the closest agreement between calculated and observed NMR chemical shifts.[64] All of the isomers prepared to date are quite reactive, but whether the most stable isomer has been observed is uncertain. Two isomeric [10]annulenes, as well as other products, are formed by photolysis of *cis*-9,10-dihydronaphthalene.[65] Neither compound exhibits properties that would suggest aromaticity. The NMR spectra are consistent with polyene structures. Both compounds are thermally unstable and revert back to stereoisomeric dihydronaphthalenes. The stereochemistry of the products is consistent with assigning the *E,Z,Z,Z,Z*- and *Z,Z,Z,Z,Z*-configurations. These results indicate that [10]annulene is sufficiently distorted from planarity that little aromatic stabilization is achieved.

[63.] R. A. King, T. D. Crawford, J. F. Stanton, and H. F. Schaefer, III, *J. Am. Chem. Soc.*, **121**, 10788 (1999).

[64.] D. R. Price and J. F. Stanton, *Org. Lett.*, **4**, 2809 (2002).

[65.] S. Masamune, K. Hojo, G. Gigam, and D. L. Rabenstein, *J. Am. Chem. Soc.*, **93**, 4966 (1971); S. Masamune and N. Darby, *Acc. Chem. Res.*, **5**, 272 (1972).
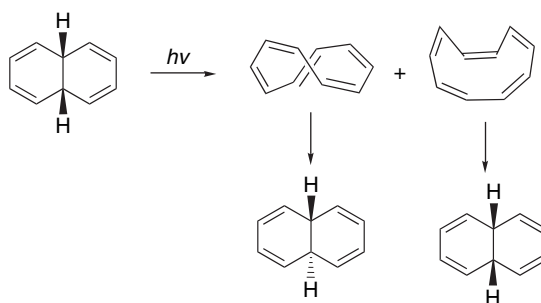
A number of structures have been prepared that avoid the steric problems associated with the 1,3,5,7,9-cyclodecapentaenes. 1,6-Methano[10]annulene (**1**) can be prepared from naphthalene in multigram quantities in four steps.[66]
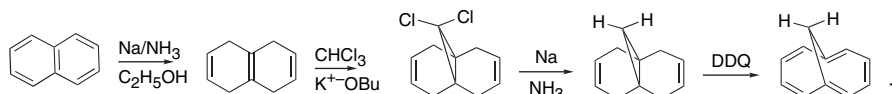
Quite a number of substituted derivatives have also been prepared. In compound **1** the steric problem is avoided with only a modest loss of planarity in the π system.[67]
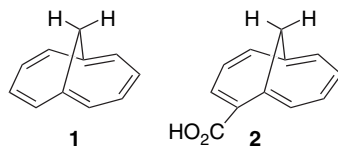
The results of X-ray crystal structure determinations on **1**[68] and its carboxylic acid derivative **2**[69] are shown in Figure 8.4. Both reveal a pattern of bond lengths that is similar to that in naphthalene (see p. 18).[70]

The NMR spectrum of compound **1** shows a diamagnetic ring current of the type expected in an aromatic system.[71] The NICS calculated for **1** is −17.7, which indicates aromaticity.[72] Both spectroscopic data and MO (MP2/DZV**) and DFT (B3LYP/6-31G) calculations indicate that the ground state of **1** is delocalized.[73] Thus while the π system in **1** is not completely planar, it appears to be sufficiently close to provide a delocalized 10-electron π system. A stabilization energy of 17.2 kcal has been obtained on the basis of an experimental heat of hydrogenation.[74]

66. E. Vogel, W. Klug, and A. Breuer, *Org. Synth.*, **VI**, 731 (1988).

67. E. Vogel and H. D. Roth, *Angew. Chem. Int. Ed. Engl.*, **3**, 228 (1964).

68. R. Bianchi, T. Pilati, and M. Simonetta, *Acta Crystallogr.*, Sect. B, **B36**, 3146 (1980).

69. M. Dobler and J. D. Dunitz, *Helv. Chim. Acta*, **48**, 1429 (1965).

70. O. Bastainsen and P. N. Skancke, *Adv. Chem. Phys.*, **3**, 323 (1961).

71. E. Vogel, *Pure Appl. Chem.*, **20**, 237 (1969).

72. M. Nendel, K. N. Houk, L. M. Tolbert, E. Vogel, H. Jiao, and P. v. R. Schleyer, *J. Phys. Chem. A*, **102**, 7191 (1998).

73. C. Gellini, P. R. Salvi, and E. Vogel, *J. Phys. Chem. A*, **104**, 3110 (2000); R. Seiler and B. Dick, *Angew. Chem. Intl. Ed. Engl.*, **48**, 4020 (2001); L. Catani, C. Gellini, and P. R. Salvi, *J. Phys. Chem. A*, **102**, 1945 (1998).

74. W. R. Roth, M. Bohm, H. W. Lennartz, and E. Vogel, *Angew. Chem. Int. Ed. Engl.*, **22**, 1007 (1983); W. R. Roth, F.-G. Klarner, G. Siepert, and H.-W. Lennartz, *Chem. Ber. Recueil.*, **125**, 217 (1992).
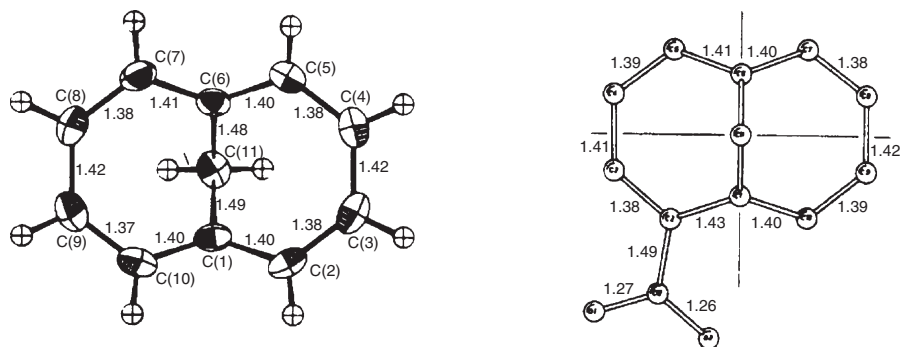
Fig. 8.4. X-ray crystal structure of 1,6-methanocyclodeca-1,3,5,7,9-pentaene (left) and 1,6-methanocyclodeca-1,3,5,7,9-pentaene-2-carboxylic acid (right). Reproduced from *Acta Crystallogr. B*, **36**, 3146 (1980) and *Helv. Chim. Acta*, **48**, 1429 (1965), by permission of the International Union of Crystallography and Wiley-VCH, respectively.

The deviation from planarity that is present in a structure such as **1** raises the question of how severely a conjugated system can be distorted from the ideal coplanar alignment of *p* orbitals and still retain aromaticity. This problem has been analyzed by determining the degree of rehybridization necessary to maximize *p*-orbital overlap in **1**.[75] A quantitative VB treatment also finds the periphery of conjugated bonds to be delocalized and the orbitals are quite similar to those in naphthalene.[76] Thus a relatively small amount of rehybridization greatly improves orbital overlap in the twisted system and stabilizes the structure.

8.2.5. [12], [14], and [16]Annulenes

[12]Annulene is a very unstable compound that undergoes cyclization to bicyclic isomers and can be kept only at very low temperature.[77] The NMR spectrum has been studied at low temperature.[78] Apart from indicating the *Z,E,Z,E,Z,E*-double-bond geometry shown in the structure, the spectrum reveals a *paramagnetic ring current*, the opposite from what is observed for aromatic systems. This feature is characteristic of the [4*n*]annulenes and has been useful in characterizing the aromaticity or lack of it in annulenes.[79]
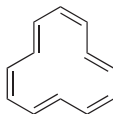
[14]Annulene was first prepared in 1960.[80] Its NMR spectrum has been investigated and shows that two geometric isomers are in equilibrium.[81]

75. R. C. Haddon, *Acc. Chem. Res.*, **21**, 243 (1988).
76. M. Sironi, M. Raimondi, D. L. Cooper, and J. Gerratt, *Theochem*, **338**, 257 (1995).
77. J. F. M. Oth, H. Rottele, and G. Schroeder, *Tetrahedron Lett.*, 61 (1970).
78. J. F. M. Oth, J.-M. Gilles, and G. Schroeder, *Tetrahedron Lett.*, 67 (1970).
79. R. C. Haddon, *Tetrahedron*, **28**, 3613, 3635 (1972).
80. F. Sondheimer and Y. Gaoni, *J. Am. Chem. Soc.*, **82**, 5765 (1960).
81. J. F. M. Oth, *Pure Appl. Chem.*, **25**, 573 (1971).

Z,E,E,Z,E,Z,E   Z,E,Z,E,Z,Z,E
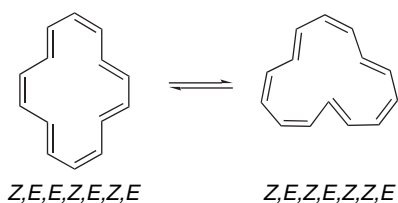
The spectrum also reveals a significant diamagnetic (aromatic) ring current. The internal hydrogens [C(3), C(6), C(10), C(13)] are very far upfield ($\delta = -0.61$ ppm).[36] The interconversion of the two forms involves a configurational change from E to Z of at least one double bond, and the E_a for this process is about 10 kcal/mol. The crystal structure for [14]annulene shows the Z,E,E,Z,E,Z,E-form to be present in the solid.[82] The bond lengths around the ring range from 1.35 to 1.41 Å, but do not show the alternating pattern of short and long bonds expected for a localized polyene. There is some distortion from planarity, especially at carbon atoms 3, 6, 10, and 13, which is caused by nonbonded repulsions between the internal hydrogens. MP2/6-31G* and B3LYP/6-31G* calculations find the delocalized structure as the only minimum.[83]

A 14-electron π system can be generated in circumstances in which the steric problem associated with the internal hydrogens of [14]annulene can be avoided. This can be achieved in 10b,10c-dihydropyrene systems, in which the annulene ring is built around a saturated core.
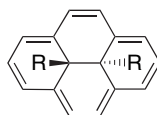
Several derivatives of this ring system have been synthesized.[84] The properties of these compounds indicate that the conjugated system has aromatic character. They exhibit NMR shifts characteristic of a diamagnetic ring current. Typical aromatic substitution reactions can be carried out.[85] An X-ray crystal structure ($R = C_2H_5$) shows that the bond lengths are in the aromatic range (1.39–1.40 Å), and there is no strong alternation around the ring.[86] The peripheral atoms are not precisely planar, but the maximum deviation from the average plane is only 0.23 Å. The dimethyl derivative is essentially planar with bond lengths between 1.38 and 1.40 Å.

Another family of 14 π-electron systems is derived from structure **3**.[87]

syn-**3**   *anti*-**3**
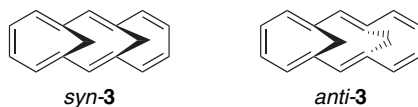
82. C. C. Chiang and I. C. Paul, *J. Am. Chem. Soc.*, **94**, 4741 (1972).
83. C. H. Choi, M. Kertesz, and A. Karpfen, *J. Am. Chem. Soc.*, **119**, 11994 (1997).
84. (a) R. H. Mitchell and V. Boekelheide, *J. Am. Chem. Soc.*, **96**, 1547 (1974); (b) V. Boekelheide and T. A. Hylton, *J. Am. Chem. Soc.*, **92**, 3669 (1970); (c) H. Blaschke, C. E. Ramey, I. Calder, and V. Boekelheide, *J. Am. Chem. Soc.*, **92**, 3675 (1970); (d) V. Boekelheide and J. B. Phillips, *J. Am. Chem. Soc.*, **89**, 1695 (1967); (e) R. H. M. Mitchell, V. S. Iyer, N. Khalifa, R. Mahadevan, S. Venugopalan, S. A. Weerawarna, and P. Zhou, *J. Am. Chem. Soc.*, **117**, 1514 (1995).
85. J. B. Phillips, R. J. Molyneux, E. Sturm, and V. Boekelheide, *J. Am. Chem. Soc.*, **89**, 1704 (1967).
86. A. W. Hanson, *Acta Crystallogr.*, **23**, 476 (1967).
87. E. Vogel, *Pure Appl. Chem.*, **28**, 355 (1971).

The *syn* isomer can achieve a conjugated system with angles of up to 35° between adjacent *p* orbitals. The *anti* isomer is much more twisted.[88] An X-ray crystal structure determination has been done on the *syn* isomer and is illustrated in Figure 8.5. It shows C−C bond lengths between 1.368 and 1.418 Å for the conjugated system.[89] The spectroscopic properties of the *syn* isomer are consistent with considering it to be a delocalized annulene.[90] B3LYP/6-31G* calculations indicate that both the *syn* and *anti* structures are stabilized by delocalization, the *syn* (17.6 kcal/mol) more so than the *anti* (8.1 kcal).[91]

An isomeric system is related to the benzenoid hydrocarbon phenanthrene. Both the *syn* and *anti* stereoisomers have been synthesized.[92]

1.45 Å   1.47 Å

1.36 Å   1.33 Å
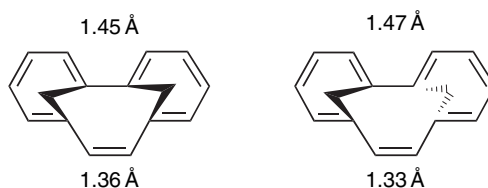
The *syn* isomer shows evidence of a diamagnetic ring current, from both the relatively low field position of the vinylic hydrogens and the upfield shift of the methylene hydrogens. The *anti* isomer shows much less pronounced shifts. The X-ray crystal structure (Figure 8.6) of the *syn* isomer shows a moderate level of bond alternation, ranging form 1.36 to 1.45 Å. In the *anti* isomer bond alternation is more pronounced with the double bond in the center ring being essentially a localized double bond.

The Hückel rule predicts nonaromaticity for [16]annulene. The compound has been synthesized and characterized.[93] The bond lengths show significant alternation in length (C=C, 1.34 Å; C−C, 1.46 Å), and the molecule is less planar

1.376 1.413 1.392 1.406 1.368
              1.394
       1.494 1.508
1.398   1.407
       1.497 1.496
1.370 1.413 1.418 1.365
       1.395 1.392

109.2 115.8 154.7 116.1 109.1
162.9   135.0   134.6   163.9
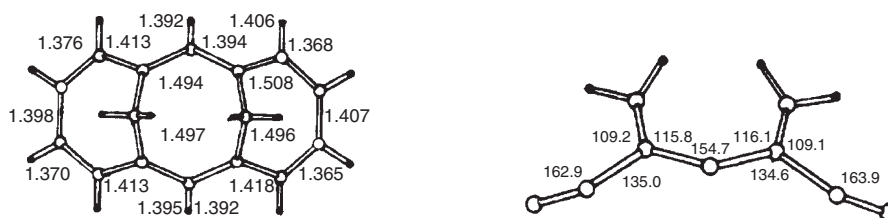
Fig. 8.5. Carbon framework from X-ray crystal structure of *syn*-tricyclo[8.4.1.1$^{3.8}$]hexadeca-1,3,5,7,9,11,13-heptaene (left). Side view showing deviation from planarity of the annulene ring (right). Reproduced from *Acta Crystallogr. B*, **33**, 940 (1977), by Permission of the International Union of Crystallography.

88. E. Vogel, J. Sombroek, and W. Wagemann, *Angew. Chem. Int. Ed. Engl.*, **14**, 564 (1975); E. Vogel, U. Haberland, and H. Gunther, *Angew. Chem. Int. Ed. Engl.*, **9**, 513 (1970).

89. R. Destro, T. Pilati, and M. Simonetta, *Acta Crystallogr.*, **B**, **33**, 940 (1977).

90. J. Dewey, H. M. Deger, W. Froehlich, B. Dick, K. A. Klingensmith, G. Hohlneicher, E. Vogel, and J. Michl, *J. Am. Chem. Soc.*, **102**, 6412 (1980).

91. M. Nendel, K. N. Houk, L. M. Tolbert, E. Vogel, H. Jiao, and P. v. R. Schleyer, *Angew. Chem. Int. Ed. Engl.*, **36**, 748 (1997).

92. E. Vogel, W. Puttmann, W. Duchatsch, T. Schieb, H. Schmickler, and J. Lex, *Angew. Chem. Int. Ed. Engl.*, **25**, 720 (1986); E. Vogel, T. Schieb, W. H. Schulz, K. Schmidt, H. Schmickler, and J. Lex, *Angew. Chem. Int. Ed. Engl.*, **25**, 723 (1986).

93. I. Calder, Y. Gaoni, and F. Sondheimer, *J. Am. Chem. Soc.*, **90**, 4946 (1968); G. Schroeder and J. F. M. Oth, *Tetrahedron Lett.*, 4083 (1966).
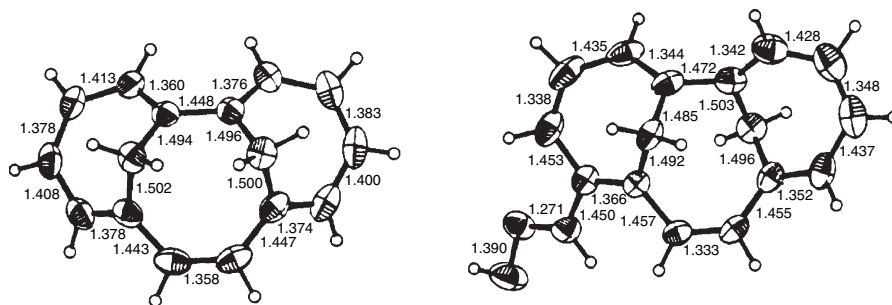
Fig. 8.6. X-ray structure of *syn*-tricyclo[8.4.1.1$^{4.9}$]hexadeca-2,4,6,8,10,12,14-heptaene (left). X-ray crystal structure of *anti* isomer of tricyclo[8.4.1.1$^{4.9}$]hexadeca-2,4,6,8,10,12,14-heptaene-5-carbaldehyde oxime (right). Reproduced from *Angew. Chem. Int. Ed. Engl.*, **25**, 720, 723 (1986), by permission of Wiley-VCH.

than [14]annulene.[94] Experimental combustion data indicate that [16]annulene is less stable than cyclooctatetraene.[95] Computational studies and NMR spectra of deuterated [16]annulene indicate that there are several conformations that differ in relative placement of the internal hydrogens.[96] These structural data are consistent with regarding [16]annulene as being nonaromatic.

8.2.6. [18]Annulene and Larger Annulenes

[18]Annulene offers a particularly significant test of the Hückel rule. The internal cavity in [18]annulene is large enough to minimize steric interaction between the internal hydrogens in a geometry that is free of angle strain. Most MO calculations find the delocalized structure to be more stable than the polyene.[97] Both MP/6-31G* and B3LYP/6-311G*calculations find a delocalized structure with D_{6h} symmetry as the minimum energy. The bond lengths are 1.39–1.42 Å , and a stabilization of 18 kcal/mol is indicated.[98]
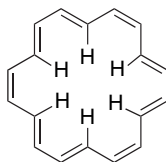
The properties of [18]annulene are consistent with its being aromatic. The X-ray crystal structure shows the molecule to be close to planarity, with the maximum deviation from the plane being 0.085 Å.[99] The bond lengths are in the range 1.385–l.405 Å, and

94. S. M. Johnson and I. C. Paul, *J. Am. Chem. Soc.*, **90**, 6555 (1968).
95. G. R. Stevenson and B. E. Forch, *J. Am. Chem. Soc.*, **102**, 5985 (1980).
96. J. M. Hernando, J. J. Quirante, and F. Enriquez, *Collect. Czech. Chem. Commun.*, **57**, 1 (1992); C. D. Stevenson and T. L. Kurth, *J. Am. Chem. Soc.*, **122**, 722 (2000).
97. J. M. Shulman and R. L. Disch, *Theochem.*, **80**, 213 (1991); K. Yoshizawa, T. Kato, and T. Yamabe, *J. Phys. Chem.*, **100**, 5697 (1996).
98. K. K. Baldridge and J. S. Siegel, *Angew. Chem. Int. Ed. Engl.*, **36**, 745 (1997); C. H. Choi, M. Kertesz, and A. Karpfen, *J. Am. Chem. Soc.*, **119**, 11994 (1997).
99. J. Bregman, F. L. Hirshfeld, D. Rabinovich, and G. M. J. Schmidt, *Acta Crystallogr.*, **19**, 227 (1965); F. L. Hirshfeld and D. Rabinovich, *Acta Crystallogr.*, **19,** 235 (1965); S. Gorter, E. Rutten-Keulemans, M. Krever, C. Romers, and D. W. J. Cruickshank, *Acta Cryst.*, **B51**, 1036 (1995).

the pattern is short, short, long, rather than alternating. The NMR spectrum indicates an aromatic ring current.[100] The chemical reactivity of the molecule also justifies its classification as aromatic.[101]

There are also examples of [18]annulene systems constructed around a saturated central core, such as in compound **4**.[102] In this compound, the internal protons are at very high field (-6 to -8 ppm), whereas the external protons are far downfield (~ 9.5 ppm).
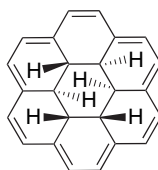
4

The chemical shift data can be used as the basis for calculating the diamagnetic ring current by comparing the value with the maximum ring current expected for a completely delocalized π system. By this criterion, the flexible [18]annulene maintains only about half (0.56) of the maximum ring current, whereas the rigid ring in **4** gives a value of 0.88, indicating more effective conjugation in this system.

The synthesis of annulenes has been carried forward to larger rings as well. [20]Annulene,[103] [22]annulene,[104] and [24]annulene[105] have all been reported. The NMR spectra of these compounds are consistent with regarding [22]annulene as aromatic, whereas the [20] and [24] analogs are not. The dominant structure for [24]annulene has a repeating *Z*,*E*,*E*-motif of double bonds. The internal hydrogens are at lower field in the ^{1}H-NMR spectrum than the external ones, which is consistent with a paramagnetic ring current. There is another minor conformation that has the same configuration of the double bonds. There is also evidence for a bond shift process that interchanges single and double bonds. This process occurs with a $\Delta G^{\ddagger}$ of about 10 kcal/mol.[106] Although the properties of these molecules have not been studied as completely as for the smaller systems, they are consistent with the predictions of the Hückel rule.

100. Y. Gaoni, A. Melera, F. Sondheimer, and R. Wolovsky, *Proc. Chem. Soc.*, 397 (1965).
101. I. C. Calder, P. J. Garratt, H. C. Longuet-Higgins, F. Sondheimer, and R. Wolovsky, *J. Chem. Soc. C*, 1041 (1967).
102. T. Otsubo, R. Gray, and V. Boekelheide, *J. Am. Chem. Soc.*, **100**, 2449 (1978).
103. B. W. Metcalf and F. Sondheimer, *J. Am. Chem. Soc.*, **93**, 6675 (1971).
104. R. M. McQuilkin, B. W. Metcalf, and F. Sondheimer, *J. Chem. Soc., Chem. Commun.*, 338 (1971).
105. I. C. Calder and F. Sondheimer, *J. Chem. Soc., Chem. Commun.*, 904 (1966).
106. J. F. M. Oth and Y. de J. de Zelicourt, *Helv. Chim. Acta*, **82**, 435 (1999).
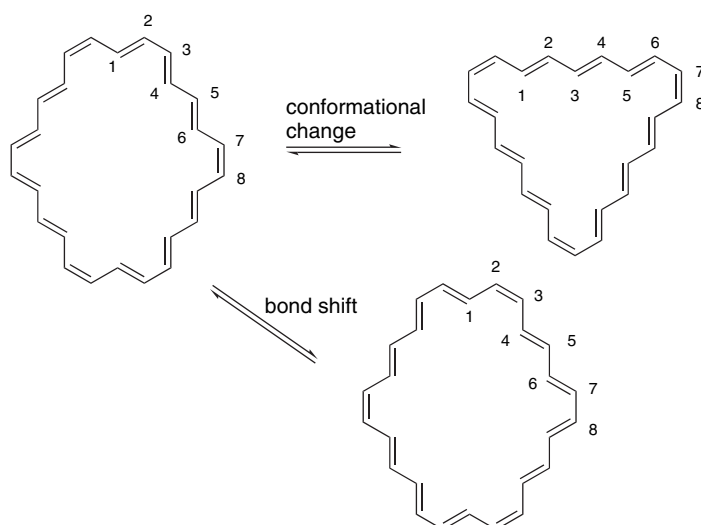
Theoretical calculations indicate that the tendency to be aromatic decreases as ring size increases.[107] For example, the NICS value decreases from –15.0 and –14.7 for [14] and [18]annulene, respectively, to –5.6 at [42]annulene and –1.2 at [66]annulene. The delocalized structures are computed to be more stable, however, leveling off at 22–23 kcal/mol at [30]annulene.[108] Of course, on a per electron basis, this means a decrease in relative stability.

8.2.7. Other Related Structures

Both clever synthesis and energetic processes leading to stable compounds have provided other examples of structures for which aromaticity might be important. Kekulene was synthesized in 1978.[109] How aromatic is this substance? By both energy and magnetic criteria, it appears that it is primarily benzenoid in character. Its energy is close to that expected from isodesmic reactions summing smaller aromatic components. Magnetic criteria, too, indicate that it is similar to the smaller polycyclic benzenoid hydrocarbons, such as phenanthrene and anthracene.[110] Kekulene seems best represented by a structure that emphasizes the aromaticity of alternating rings, similar to the structure of phenanthrene (see p. 772). (See Problem 8.15 to consider this issue more thoroughly.)

[107.] C. H. Choi and M. Kertesz, *J. Chem. Phys.*, **108**, 6681 (1998).

[108.] C. S. Wannere and P. v. R. Schleyer, *Org. Lett.*, **5**, 865 (2003).

[109.] H. A. Staab and F. Diedrich, *Angew. Chem. Int. Ed. Engl.*, **17**, 372 (1978); H. A. Staab and F. Diedrich, *Chem. Ber.*, **116**, 3487 (1983).

[110.] H. Jiao and P. v. R. Schleyer, *Angew. Chem. Int. Ed. Engl.*, **35**, 2383 (1996).

Kekulene
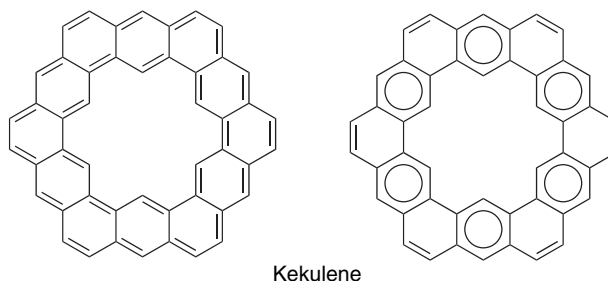
Fullerene, C_{60}, is a spherical form of carbon that is produced by processes such as laser vaporization of graphite.[111] The structure consists of hexagons and pentagons, corresponding to the pattern of a soccer ball. There is bond length variation with the bonds shared by the hexagonal rings being shorter ($1.40 \pm 0.01\,\text{Å}$) than those of the pentagons ($1.46 \pm 0.01\,\text{Å}$). Unlike benzene, with its two-Kekule structure, there is only one valence bond structure for C_{60}. It has double bonds at all hexagon-hexagon edges and single bonds at the pentagonal edges. An isodesmic energy computation suggests that the π system is substantially less stable than for benzene on an atom-by-atom comparison.[112] Calculated chemical shift parameters suggest that the five-membered rings are antiaromatic, whereas the hexagonal rings are aromatic.[113] Thus it appears that fullerene is a delocalized molecule, but with both stabilizing and destabilizing components, which are partially compensating in terms of stabilization energy.

It was pointed out that a different array of atomic orbitals might be conceived of in large conjugated rings. The array, called a *Mobius twist*, results in there being one point in the ring at which the atomic orbitals have a phase reversal (node).[114]
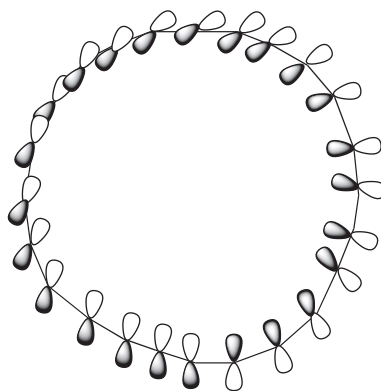
If the ring were sufficiently large that the twist between individual orbitals was small, such a system would not necessarily be less stable than the normal array of atomic orbitals. This same analysis points out that in such an array the Hückel rule is reversed and aromaticity is predicted for the $4n$ π-electron systems.

111. H. W. Kroto, J. P. Heath, S. C. O'Brien, R. F. Curl, and R. E. Smalley, *Nature*, **318**, 162 (1985).
112. P. W. Fowler, D. J. Collins, and S. J. Austin, *J. Chem. Soc., Perkin Trans. 2*, 275 (1993).
113. P. v. R. Schleyer, C. Maerker, A. Dransfeld, H. Jiao, and N. J. R. van Eikema Hommes, *J. Am. Chem. Soc.*, **118**, 6317 (1996).
114. E. Helibronner, *Tetrahedron Lett.*, 1923 (1964).
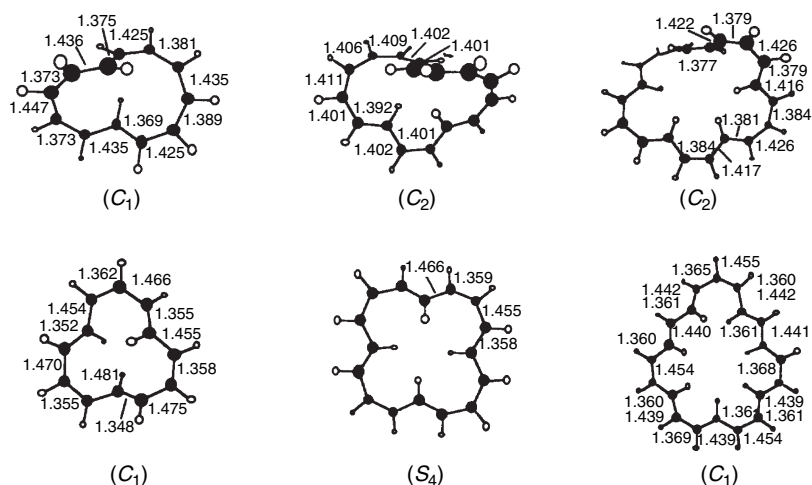
Fig. 8.7. Most stable (top) and most aromatic (bottom) Mobius structures for [12], [16], and [20]annulene. Reproduced from *Org. Lett.*, **4**, 3431 (2002), by permission of the American Chemical Society.

The possibility of Mobius conjugation in [12], [16], and [20]annulene has been explored using B3LYP/6-31G* calculations.[115] The most stable and most aromatic structures are shown in Figure 8.7. The most aromatic Mobius isomer of [12]annulene is found about 4.4 kcal/mol above the most stable structure. It shows an NICS of −14.6 and relatively little bond length alternation, despite angles deviating as much as 53.6° from the alignment of the *p* orbitals. The most stable structure does not have aromatic characteristics, showing a positive NICS. For [16]annulene, the most aromatic Mobius structure is 15.8 kcal/mol above the most stable structure. The most aromatic structure for [20]annulene is 6.2 kcal/mol above the most stable structure. Thus, although it appears that there are energy minima corresponding to Mobius structures, they all lie above nonaromatic structures in energy.

Comparison of Properties of "Most Stable" and "Most Aromatic" Structure for [12], [16], and [20]annulenes

	[12]		[16]		[20]	
	Most stable	Best Mobius	Most stable	Best Mobius	Most stable	Best Mobius
Relative energy[a]	0.0	4.4	0.0	15.8	0.0	6.2
Δ in bond length[b]	0.133	0.078	0.097	0.019	0.095	0.049
NICS	+3.2	−14.6	+10.9	−14.5	+12.1	−10.2
χ	−65.0	−101.5	−63.9	−176.8	−75.6	−170.8
Max angle of twist	62.4°	53.6°	32.6°	29.1°	29.5°	29.9°

a. kcal/mol.
b. Difference between shortest and longest bond lengths in Å.

So far, no ground state molecule in which the twisted conjugation exists has been made. Whatever stabilization is associated with aromaticity in the Mobius structures is

[115.] C. Castro, C. Isborn, W. L. Karney, M. Mauksch, and P. v. R. Schleyer, *Org. Lett.*, **4**, 3431 (2002).

counterbalanced by bond angle and other strain, so the prediction of Mobius aromaticity remains to be verified experimentally. Its correctness is strongly suggested, however, by the fact that transition structures with twisted orbital arrays appear to be perfectly acceptable in many organic reactions.[116] We return to this topic in Section 10.1. The rules for aromaticity can be generalized to include Mobius orbital arrays:

Hückel Orbital Array	Mobius Orbital Array
$4n + 2 =$ Aromatic	$4n =$ Aromatic
$4n =$ Antiaromatic	$4n + 2 =$ Antiaromatic

8.3. Aromaticity in Charged Rings

There are striking stability relationships owing to aromaticity in charged ring systems. The HMO energy levels that apply to fully conjugated planar three- to nine-membered rings were shown earlier in Figure 8.1 (p. 714). These energy levels are applicable to ions as well as to the neutral annulenes. A number of cations and anions that are completely conjugated planar structures are shown in Scheme 8.1. Among these species, the Hückel rule predicts aromatic stability for cyclopropenium ion (**A**), cyclobutadiene dication (**C**), cyclobutadiene dianion (**D**), cyclopentadienide anion (**F**), cycloheptatrienyl cation (tropylium ion, **G**), the dications and dianions derived from cyclooctatetraene (**I, J**) and the cyclononatetraenide anion (**K**). The other species shown, which have $4n$ π electrons, are expected to be quite unstable. These include cyclopropenide anion (**B**), cyclopentadienyl cation (**E**), and cycloheptatrienide (**H**). Let us examine what is known about the chemistry of some of these systems.

There is a good deal of information about the cyclopropenium ion that supports the idea that it is exceptionally stable. It and a number of derivatives can be generated by ionization procedures.

Scheme 8.1. Conjugated Cyclic Cations and Anions
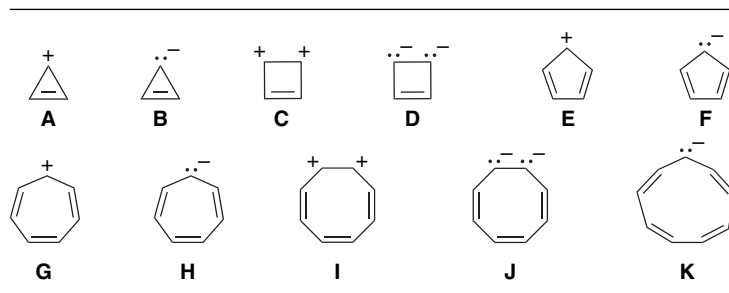
116. H. E. Zimmerman, *J. Am. Chem. Soc.*, **88**, 1566 (1966); H. E. Zimmerman, *Acc. Chem. Res.*, **4**, 272 (1971).
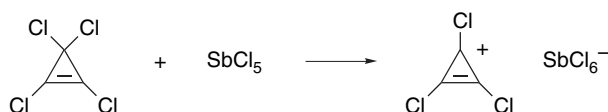
Ref. 117
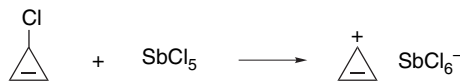
Ref. 118

The 1,2,3-tri-*t*-butylcyclopropenium cation is so stable that the perchlorate salt can be recrystallized from water.[119] An X-ray study of triphenylcyclopropenium perchlorate has verified the existence of the carbocation as a discrete ion.[120] Quantitative estimation of the stability of the unsubstituted cyclopropenium ion can be made in terms of its pK_{R^+} value of -7.4, which is intermediate between such highly stabilized ions as triphenylmethyl cation and the *bis*-(4-methoxyphenyl)methyl cation.[121] (See Section 4.4.1 for the definition of pK_{R^+}). An HF/6-31G* MO calculation on the following isodesmic reaction:

yields a ΔH of $+38.2$ kcal/mol, whereas experimental data on the heats of formation of the various species give $\Delta H = +31$ kcal/mol.[122] Both values imply that the cyclopropenium ion is much more stable than the allyl cation. G2 calculations indicate total aromatic stabilization of 59.1 kcal/mol based on the reaction[123]
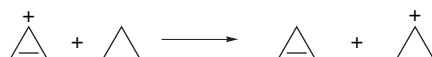
A radical-based homodesmotic reaction gives a value of 30.4 kcal/mol, which compares with 29.1 kcal/mol for benzene by the same approach.[124] The gas phase heterolytic bond dissociation energy to form cyclopropenium ion from cyclopropene is 225 kcal/mol. This compares with 256 kcal/mol for formation of the allyl cation from propene and 268 kcal/mol for the 1-propyl cation from propane.[125] It is clear that the cyclopropenyl cation is highly stabilized.

In contrast, the less strained four π-electron cyclopentadienyl cation is quite unstable, being calculated to have a negative stabilization of 56.7 kcal/mol.[126] The

[117.] S. W. Tobey and R. West, *J. Am. Chem. Soc.*, **86**, 1459 (1964); R. West, A. Sado, and S. W. Tobey, *J. Am. Chem. Soc.*, **88**, 2488 (1966).

[118.] R. Breslow, J. T. Groves, and G. Ryan, *J. Am. Chem. Soc.*, **89**, 5048 (1967).

[119.] J. Ciabattoni and E. C. Nathan, III, *J. Am. Chem. Soc.*, **91**, 4766 (1969).

[120.] M. Sundaralingam and L. H. Jensen, *J. Am. Chem. Soc.*, **88**, 198 (1966).

[121.] R. Breslow and J. T. Groves, *J. Am. Chem. Soc.*, **92**, 984 (1970).

[122.] L. Radom, P. C. Hariharan, J. A. Pople, and P. v. R. Schleyer, *J. Am. Chem. Soc.*, **98**, 10 (1976).

[123.] M. N. Glukhovtsev, S. Laiter, and A. Pross, *J. Phys. Chem.*, **100**, 17801 (1996).

[124.] C. H. Suresh and N. Koga, *J. Org. Chem.*, **67**, 1965 (2002).

[125.] F. P. Lossing and J. L. Holmes, *J. Am. Chem. Soc.*, **106**, 6917 (1984).

[126.] P. v. R. Schleyer, P. K. Freeman, H. Jiao, and B. Goldfuss, *Angew. Chem. Int. Ed. Engl.*, **34**, 337 (1995); B. Reidl and P. v. R. Schleyer, *J. Comput. Chem.*, **19**, 1402 (1998).

cyclopentadienyl cation is also calculated to be antiaromatic by magnetic susceptibility and chemical shift criteria.[127] Its pK_{R+} has been estimated as –40, using an electrochemical cycle.[128] The heterolytic bond dissociation energy to form the cation from cyclopentadiene is 258 kcal/mol, which is substantially more than for formation of an allylic cation from cyclopentene but only slightly more than the 252 kcal/mol required for formation of an unstabilized secondary carbocation.[125] The high energy of the cyclopentadienyl cation is also indicated by ionization studies in solution. A rate retardation of 10^{-14} relative to cyclopentyl analogs has been estimated from solvolytic rate data.[129] Solvolysis of cyclopentadienyl halides assisted by silver ion is extremely slow, even though the halide is doubly allylic.[130] When cyclopentadienyl bromide and antimony pentafluoride react at $-78°C$, an EPR spectrum is observed, which indicates that the cyclopentadienyl cation is a triplet.[131] Similar studies indicate that the pentaisopropyl[132] and pentachlorocyclopentadienyl cation are also triplets, but the ground state of the pentaphenyl derivative is a singlet.

The relative stability of the anions derived from cyclopropene and cyclopentadiene by deprotonation is just the reverse of the situation for the cations. Cyclopentadiene is one of the most acidic hydrocarbons known, with a pK_a of 16.0.[133] The pK's of triphenylcyclopropene and trimethylcyclopropene have been estimated as 50 and 62, respectively, using electrochemical cycles[134] (see Section 6.1). The unsubstituted compound would be expected to fall somewhere between and thus must be about 40 powers of 10 less acidic than cyclopentadiene. MP2/6-311+G($2df$,$2pd$) and B3LYP/6-311+G($2df$,$2pd$) calculations indicate a small destabilization of the cyclopropenyl anion, relative to the cyclopropyl anion.[135] Thus the six π-electron cyclopentadienide anion is enormously stabilized relative to the four π-electron cyclopropenide ion, in agreement with the Hückel rule.

The Hückel rule predicts aromaticity for the six π-electron cation derived from cycloheptatriene by hydride abstraction and antiaromaticity for the planar eight π-electron anion that would be formed by deprotonation. The cation is indeed very stable, with a pK_{R+} of +4.7.[136] Salts containing the cation can be isolated as a result of a variety of preparative procedures.[137] On the other hand, the pK of cycloheptatriene has been estimated at 36.[134] This value is similar to normal 1,4-dienes and does not indicate strong destabilization. The seven-membered eight π-electron anion is probably nonplanar. This would be similar to the situation in the nonplanar eight π-electron hydrocarbon, cyclooctatetraene.

127. H. Jiao, P. v. R. Schleyer, Y. Mo, M. A. McAllister, and T. T. Tidwell, *J. Am. Chem. Soc.*, **119**, 7075 (1997).
128. R. Breslow and S. Mazur, *J. Am. Chem. Soc.*, **95**, 584 (1975).
129. A. D. Allen, M. Sumonja, and T. T. Tidwell, *J. Am. Chem. Soc.*, **119**, 2371 (1997).
130. R. Breslow and J. M. Hoffman, Jr., *J. Am. Chem. Soc.*, **94**, 2110 (1972).
131. M. Saunders, R. Berger, A. Jaffe, J. M. McBride, J. O'Neill, R. Breslow, J. M. Hoffman, Jr., C. Perchonock, E. Wasserman, R. S. Hutton, and V. J. Kuck, *J. Am. Chem. Soc.*, **95**, 3017 (1973).
132. H. Sitzmann, H. Bock, R. Boese, T. Dezember, Z. Havlas, W. Kaim, M. Moscherosch, and L. Zanathy, *J. Am. Chem. Soc.*, **115**, 12003 (1993).
133. A. Streitwieser, Jr., and L. L. Nebenzahl, *J. Am. Chem. Soc.*, **98**, 2188 (1976).
134. R. Breslow and W. Chu, *J. Am. Chem. Soc.*, **95**, 411 (1973).
135. G. N. Merrill and S. R. Kass, *J. Am. Chem. Soc.*, **119**, 12322 (1997).
136. W. v. E. Doering and L. H. Knox, *J. Am. Chem. Soc.*, **76**, 3203 (1954).
137. T. Nozoe, *Prog. Org. Chem.*, **5**, 132 (1961); K. M. Harmon, in *Carbonium Ions*, Vol. IV, G. A. Olah and P. v. R. Schleyer, eds., Wiley-Interscience, New York, 1973, Chap. 2.

The cyclononatetraenide anion is generated by treatment of the halide **5** with lithium metal.[138]

5
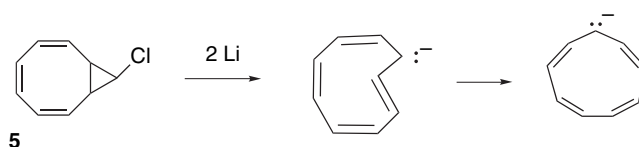
An isomeric form of the anion that is initially formed is converted to the all-*cis* system rapidly at room temperature.[139] Data on the equilibrium acidity of the parent hydrocarbon are not available, so the stability of the anion cannot be judged quantitatively. The NMR spectrum of the anion, however, is indicative of aromatic character.[139b]

Several doubly charged ions are included in Scheme 8.1; some have been observed experimentally. Ionization of 3,4-dichloro-1,2,3,4-tetramethylcyclobutene in SbF_5-SO_2 at $-75°C$ results in an NMR spectrum attributed to the tetramethyl derivative of the cyclobutadienyl dication.[140]
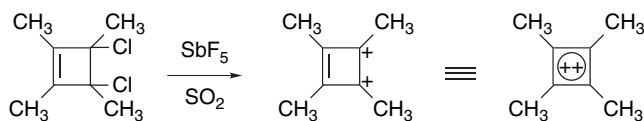
It is difficult to choose a reference compound against which to judge the stability of the dication. That it can be formed at all, however, is suggestive of special stabilization associated with the two π-electron system. The dianion formed by adding two electrons to the π system of cyclobutadiene also meets the $4n + 2$ criterion. In this case, however, four of the six electrons would occupy HMO nonbonding orbitals, so high reactivity could be expected. There is some evidence that this species may have a finite existence.[141] Reaction of 3,4-dichlorocyclobutene with sodium naphthalenide, followed a few minutes later by methanol-O-*d* gives a low yield of 3,4-di-deutero-cyclobutene. The inference is that the dianion $[C_4H_4^{2-}]$ is present, but there has not yet been direct experimental observation of this species. Cyclooctatetraene is reduced by alkali metals to a dianion.
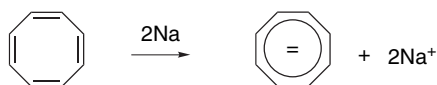
The NMR spectrum is indicative of a planar aromatic structure.[142] The NICS value (MP2/6-31G*) is -19.9.[143] It has been demonstrated that the dianion is more stable

[138] T. J. Katz and P. J. Garratt, *J. Am. Chem. Soc.*, **86**, 5194 (1964); E. A. LaLancette and R. E. Benson, *J. Am. Chem. Soc.*, **87**, 1941 (1965).

[139] (a) G. Boche, D. Martens, and W. Danzer, *Angew. Chem. Inter. Ed. Engl.*, **8,** 984 (1969); (b) S. Fliszar, G. Cardinal, and M. Bernaldin, *J. Am. Chem. Soc.*, **104**, 5287 (1982); S. Kuwajima and Z. G. Soos, *J. Am. Chem. Soc.*, **108**, 1707 (1986).

[140] G. A. Olah, J. M. Bollinger, and A. M. White, *J. Am. Chem. Soc.*, **91**, 3667 (1969); G. A. Olah and G. D. Mateescu, *J. Am. Chem. Soc.*, **92**, 1430 (1970).

[141] J. S. McKennis, L. Brener, J. R. Schweiger, and R. Pettit, *J. Chem. Soc., Chem. Commun.*, 365 (1972).

[142] T. J. Katz, *J. Am. Chem. Soc.*, **82**, 3784 (1960).

[143] P. v. R. Schleyer, C. Maerker, A. Dransfeld, H. Jiao, and J. R. van Eikema Hommes, *J. Am. Chem. Soc.*, **118**, 6317 (1996).

than the radical anion formed by one-electron reduction, since the radical anion dispro-portionates to cyclooctatetraene and the dianion.
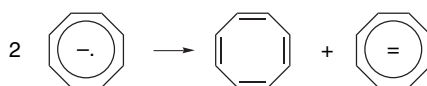
The crystal structure of the potassium salt of 1,3,5,7-tetramethylcyclootatetraene dianion has been determined by X-ray diffraction.[144] The eight-membered ring is planar, with "aromatic" C–C bond lengths of about 1.41 Å without significant alter-nation. Spectroscopic and structural studies lead to the conclusion that the cycloocc-tatetraene dianion is a stabilized delocalized structure.

A dication derived from 1,3,5,7-tetramethylcyclooctatetraene is formed at $-78°C$ in SO_2Cl by reaction with SbF_5. Both the proton and carbon NMR spectra indicate that the ion is a symmetrical, diamagnetic species, and the chemical shifts are consistent with an aromatic anisotropy. At about $-20°C$, this dication undergoes a chemical transformation to a more stable diallylic dication.[145]
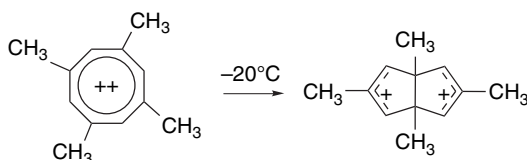
Reduction of the nonaromatic polyene [12]annulene, either electrochemically or with lithium metal, generates a 14 π-electron dianion.[146]
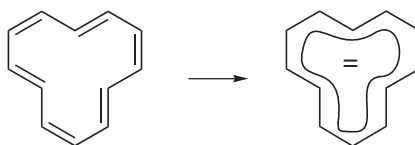
The NMR spectrum of the resulting dianion shows chemical shifts indicative of aromatic character, even though steric interactions among the internal hydrogens must prevent complete coplanarity. In contrast to the neutral [12]annulene, which is thermally unstable above – 50°C, the dianion remains stable at 30°C. The dianion of [16]annulene has also been prepared, and shows properties consistent with its being regarded as aromatic.[147]

The pattern of experimental results on charged species with cyclic conjugated systems is summarized in Table 8.1. It is consistent with the applicability of Hückel's rule to charged, as well as neutral, conjugated planar cyclic structures.

144. S. Z. Goldberg, K. N. Raymond, C. A. Harmon, and D. H. Templeton, *J. Am. Chem. Soc.*, **96**, 1348 (1974).
145. G. A. Olah, J. S. Staral, G. Liang, L. A. Paquette, W. P. Melega, and M. J. Carmody, *J. Am. Chem. Soc.*, **99**, 3349 (1977).
146. J. F. M. Oth and G. Schroeder, *J. Chem. Soc. B*, 904 (1971).
147. J. F. M. Oth, G. Anthoine, and J. -M. Gilles, *Tetrahedron Lett.*, 6265 (1968).

Table 8.1. Hückel's Rule Relationships for Charged Species

Compound	π Electrons
Aromatic	
Cyclopropenylium ion	2
Cyclopentadienide anion	6
Cycloheptatrienylium ion	6
Cyclooctatetraene dianion	10
Cyclononatetraenide anion	10
[12]Annulene dianion	14
Antiaromatic	
Cyclopropenide anion	4
Cyclopentadienylium ion	4
Nonaromatic	
Cycloheptatrienide anion	8

8.4. Homoaromaticity

Homoaromaticity is a term used to describe systems in which a stabilized cyclic conjugated system is formed by bypassing one saturated atom.[148] One would expect the resulting stabilization to be reduced because of poorer overlap of the orbitals, but the properties of several such cationic species suggest that there is substantial stabilization. The cyclooctatrienyl cation (homotropylium **6**) is an example.
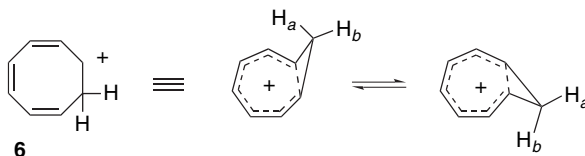
A significant feature of the NMR spectrum of this cation is the fact that the protons *a* and *b* exhibit sharply different chemical shifts. Proton *a* is 5.8 ppm upfield of *b*, indicating the existence of a diamagnetic ring current.[149] The fact that the two protons exhibit separate signals also establishes that there is a substantial barrier for the conformational process that interchanges H_a and H_b. The $\Delta G^{\ddagger}$ for this process is 22.3 kcal/mol.[150] MO (MP3/6-31G*) calculations that include the effects of electron correlation indicate that the homoconjugated structure is a good description of the cation and find that there is a strong aromatic ring current.[151] MP4(SDQ)/6-31G(*d*) calculations were used to compare the homoaromatic structure with a planar model. The computations indicate that the total energy difference between the two structures includes a homoaromatic stabilization of about 4 kcal/mol and that additional strain in

148. S. Winstein, *Q. Rev. Chem. Soc.*, **23**, 141 (1969); L. A. Paquette, *Angew. Chem. Int. Ed. Engl.*, **17**, 106 (1978); R. V. Williams, *Adv. Phys. Org. Chem.*, **29**, 273 (1994); R. V. Williams, *Chem. Rev.*, **101**, 1185 (2001).
149. (a) P. Warner, D. L. Harris, C. H. Bradley, and S. Winstein, *Tetrahedron Lett.*, 4013 (1970); C. E. Keller and R. Pettit, *J. Am. Chem. Soc.*, **88**, 604, 606 (1966); R. F. Childs, *Acc. Chem. Res.*, **17**, 347 (1984); (b) R. C. Haddon, *J. Am. Chem. Soc.*, **110**, 1108 (1988).
150. S. Winstein, C. G. Kreiter, and J. I. Brauman, *J. Am. Chem. Soc.*, **88**, 2047 (1966).
151. R. C. Haddon, *J. Am. Chem. Soc.*, **110**, 1108 (1988).

the planar structure accounts for most of the difference.[152] A higher estimate of the homoaromatic stabilization of 13.4 kcal/mol results from a calculation that assigns the difference in strain as 10.1 kcal/mol.[153]

The cyclobutenyl cation **7** is the homoaromatic analog of the very stable cyclopropenium cation. This ion can be prepared from 3-acetoxycyclobutene using "superacid" conditions.[154]
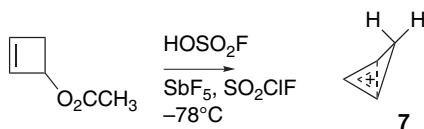
The homoaromatic cyclobutenylium ion is calculated to be 10.3 kcal/mol less stable than the isomeric methylcyclopropenylium ion, but the barrier for interconversion is high.[155] The temperature-dependent NMR spectrum of the ion can be analyzed to show that there is a barrier (8.4 kcal/mol) for the ring flip that interchanges the two hydrogens of the methylene group. The ^{13}C-NMR chemical shift is also compatible with the homoaromatic structure. MO (MP3/6-31G*) calculations are successful in reproducing the structural and spectroscopic characteristics of the cation and are consistent with a homoaromatic structure.[156] Analysis of electron density did not find a bond critical point between C(1) and C(3), but the electron density is equivalent to a bond order of about 0.45. The electron density contours are shown in Figure 8.8.

The existence of stabilizing homoconjugation in anions has been more difficult to establish. Much of the discussion has revolved about anion **8**. The species was proposed to have aromatic character on the basis of the large upfield shift of the CH_2 group, which would lie in the shielding region generated by a diamagnetic ring current.[157] The ^{13}C-NMR spectrum can also be interpreted in terms of homoaromaticity.[158] Both
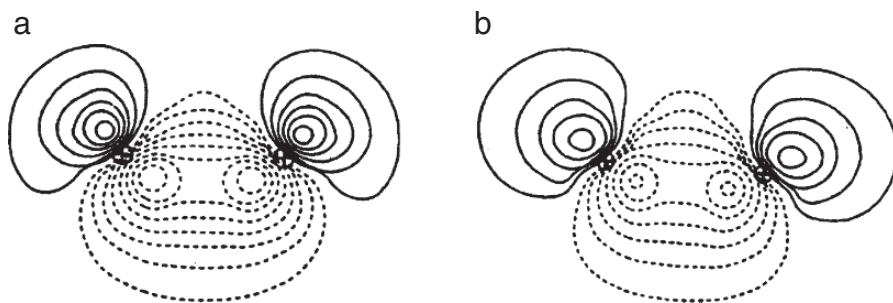
Fig. 8.8. Electron density contours for C(1)–C(3) bridging in homoaromatic cations: (a) cyclobutenylium ion; (b) cyclooctatrienylium ion. Reproduced from *J. Phys. Org. Chem.*, **6**, 445 (1993).

[152]. D. Cremer, F. Reichel, and E. Kraka, *J. Am. Chem. Soc.*, **113**, 9459 (1991).

[153]. B. Reindl, T. Clark, and P. v. R. Schleyer, *J. Phys. Chem. A*, **102**, 8953 (1998).

[154]. G. A. Olah, J. S. Staral, R. J. Spear, and G. Liang, *J. Am. Chem. Soc.*, **97**, 5489 (1975).

[155]. A. Cunje, C. F. Rodriquez, M. H. Lien, and A. C. Hopkinson, *J. Org. Chem.*, **61**, 5212 (1996).

[156]. R. C. Haddon and K. Raghavachari, *J. Am. Chem. Soc.*, **105**, 1188 (1983); M. Schindler, *J. Am. Chem. Soc.*, **109**, 1020 (1987); S. Sieber, P. v. R. Schleyer, A. H. Otto, J. Gauss, F. Reichel, and D. Cremer, *J. Phys. Org. Chem.*, **6**, 445 (1993).

[157]. S. Winstein, M. Ogliaruso, M. Sakai, and J. M. Nicholson, *J. Am. Chem. Soc.*, **89**, 3656 (1967).

[158]. M. Cristl, H. Leininger, and D. Brueckner, *J. Am. Chem. Soc.*, **105**, 4843 (1983).
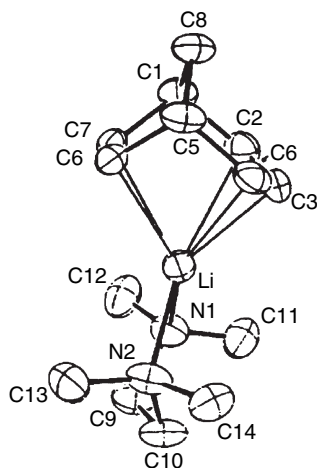
Fig. 8.9. Crystal structure of the TMEDA complex of lithium bicyclo[3.2.1]octa-2,6-dienide. Reproduced from *Angew. Chem. Int. Ed. Engl.*, **25**, 468 (1986), by permission of Wiley-VCH.

gas phase and solution measurements suggest that the parent hydrocarbon is more acidic than would be anticipated if there were no special stabilization of the anion.[159] An X-ray crystal structure of the lithium salt has been done.[160] The structure is a monomeric TMEDA complex (Fig. 8.9). The lithium is not symmetrically disposed toward the anion but is closer to one carbon of the allyl system. There is no indication of flattening of the homoconjugated atoms and the C(6)–C(7) bond distance is in the normal double-bond range (1.354 Å).

In contrast to the homoaromatic cations **6** and **7**, MO calculations fail to reveal substantial stabilization of the anion **8**.[161] There does not seem to be any diamagnetic ring current associated with the anion.[162] The weight of the evidence seems to be against significant homoaromatic stabilization in **8**.

8
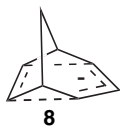
8.5. Fused-Ring Systems

Many completely conjugated hydrocarbons can be built up from benzene, the other annulenes and related structural fragments. Scheme 8.2 gives the structures, names, and stabilization energies of a variety of such hydrocarbons. Derivatives of
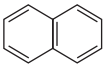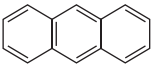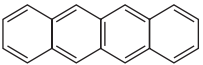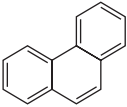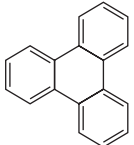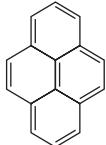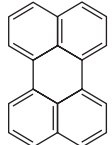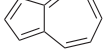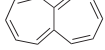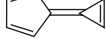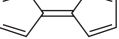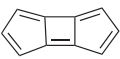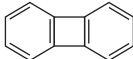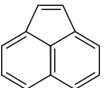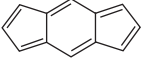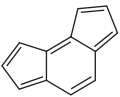
[159] R. E. Lee and R. R. Squires, *J. Am. Chem. Soc.*, **108**, 5078 (1986); W. N. Washburn, *J. Org. Chem.*, **48**, 4287 (1983).

[160] N. Hertkorn, F. H. Kohler, G. Mueller, and G. Reber, *Angew. Chem. Int. Ed. Engl.*, **25**, 468 (1986).

[161] J. B. Grutzner and W. L. Jorgenson, *J. Am. Chem. Soc.*, **103**, 1372 (1981); E. Kaufman, H. Mayr, J. Chandrasekhar, and P. v. R. Schleyer, *J. Am. Chem. Soc.*, **103**, 1375 (1981); R. Lindh, B. O. Roos, G. Jonsall, and P. Ahlberg, *J. Am. Chem. Soc.*, **108**, 6554 (1986).

[162] N. H. Werstiuk and J. Ma, *Can. J. Chem.*, **77**, 752 (1999).

Scheme 8.2. Stabilization Energies of Some Polycyclic Hydrocarbons[a]

	Benzene	Naphthalene	Anthracene	Naphthacene
HMO	2.00	3.698	5.31	6.93
HMO'	0.39	0.55	0.66	0.76
RE	0.38	0.59	0.71	0.83
SCF-MO	0.869 eV	1.323 eV	1.600 eV	1.822 eV

	Phenanthrene	Triphenylene	Pyrene	Perylene
HMO	5.44	7.27	6.50	8.24
HMO'	0.72	1.01	0.82	0.96
RE	0.85	1.13	0.95	1.15
SCF-MO	1.933 eV	2.654 eV	2.10 eV	2.619 eV

	Butalene	Pentalene	Azulene	Heptalene
HMO	1.66	2.45	3.25	3.61
HMO'	−0.48	−0.14	0.23	−0.04
RE	−0.34	−0.09	0.27	−0.01
SCF-MO	−0.28 eV	−0.006 eV	0.169 eV	−0.004 eV

	Methylene-cyclopropene	Fulvene	Calicene	Fulvalene
HMO	0.96	1.46	–	2.80
HMO'	0.02	−0.012	0.34	−0.33
RE		−0.01	0.39	−0.29
SCF-MO				

	Benzo-cyclobutadiene		Biphenylene	Acenaphthene
HMO	2.38	–	4.50	4.61
HMO'	−0.22	−0.22	0.32	0.47
RE	−0.16	–	0.42	0.57
SCF-MO	–	–	1.346 ev	1.335 ev

	s-indacene	*as*-indacene
HMO'	0.110	−0.249

a. Stabilization energies are from the following sources: HMO: C. A. Coulson, A. Streitwieser, Jr., M. D. Poole, and J. I. Brauman, *Dictionary of π-Electron Calculations*, W. H. Freeman, San Francisco, 1965.
 HMO′: B. A. Hess, Jr., and L. J. Schaad, Jr., *J. Am. Chem. Soc.*, **93**, 305, 2413 (1971); *J. Org. Chem.*, **36**, 3418 (1971); *J. Org. Chem.*, **37**, 4179 (1972).
 RE: A. Moyano and J. C. Paniagua, *J. Org. Chem.*, **51**, 2250 (1986).
 SCF-MO: M. J. S. Dewar and C. de Llano, *J. Am. Chem. Soc.*, **91**, 789 (1969); 1 eV = 23 kcal/mol.

these hydrocarbons having heteroatoms in place of one or more carbon atoms constitute another important class of organic compounds and are discussed in Section 8.6. It is of interest to be able predict the stability of such fused-ring compounds. Because Hückel's rule applies only to monocyclic systems, it cannot be applied to the fused-ring compounds, but there have been many efforts to develop relationships that would predict their stability. The underlying concepts are the same as for monocyclic systems; stabilization results from a particularly favorable arrangement of MOs, whereas instability is associated with unpaired electrons or electrons in high-energy orbitals.

The same approximations discussed in Section 1.5 permit calculation of the HMO for conjugated systems of the type shown in Scheme 8.2, and many of the results have been tabulated.[163] However, attempts to correlate stability with the Hückel delocalization energy relative to isolated double bonds give poor correlation with the observed chemical properties of the compounds.

Much better agreement between calculated stabilization energy and experimental chemical properties is achieved when a polyene is chosen as the reference state.[164] A series of energy terms corresponding to the structural units in the reference polyene was established empirically by Hess and Schaad.[165] The difference between the energy of the conjugated hydrocarbon by HMO calculations and the sum of the appropriate structural units gives a stabilization energy. For azulene, for example, the HMO calculation gives an energy of $10\alpha + 13.36\beta$. The energy for the polyene reference is obtained by summing contributions for the component bond types: $3(CH{=}CH) + 2(HC{=}C) + 3(HC{-}CH) + 1(C{-}C) = 13.13\beta$. The difference, 0.23β, is the stabilization or resonance energy assigned to azulene by this method. For comparison of nonisomeric molecules, the Hess-Schaad treatment uses resonance energy per electron, which is obtained by dividing the calculated stabilization energy by the number of π electrons. Although the resulting stabilization energies are based on a rudimentary HMO calculation, they are in good qualitative agreement with observed chemical stability. The stabilizations have been calculated for most of the molecules in Scheme 8.2 and are listed as HMO'.

The energy parameters assigned to the reference polyene used by Hess and Schaad were developed on an empirical basis. Subsequently Moyano and Paniagua developed an alternative set of reference bond energies on a theoretical basis,[166] and these values are shown along with the Hess-Schaad values in Table 8.2. The stabilizations calculated for the various hydrocarbons using this point of reference in Scheme 8.2 are those listed as RE (for resonance energy). The Hess-Schaad HMO' and the RE values are in generally good agreement with observed stability. Both calculations give negative stabilization for benzocyclobutadiene, for example.[167]

The values listed in Scheme 8.2 as SCF-MO are from an early semiempirical SCF calculation, which was the first instance in which a polyene was chosen as the reference state.[164]

163. E. Heilbronner and P. A. Straub, *Hückel Molecular Orbitals*, Springer-Verlag, Berlin, 1966; C. A. Coulson and A. Streitwieser, *Dictionary of π-Electron Calculations*, W. H. Freeman, San Francisco, 1965.

164. M. J. S. Dewar and C. de Llano, *J. Am. Chem. Soc.*, **91**, 789 (1969).

165. B. A. Hess, Jr., and L. J. Schaad, *J. Am. Chem. Soc.*, **93**, 305, 2413 (1971); *J. Org. Chem.*, **36**, 3418 (1971); *J. Org. Chem.*, **37**, 4179 (1972).

166. A. Moyano and J. C. Paniagua, *J. Org. Chem.*, **51**, 2250 (1986).

167. There are a number of other systems for comparing the stability of conjugated cyclic compounds with reference polyenes. For example, see L. J. Schaad and B. A. Hess, Jr., *Pure Appl. Chem.*, **54**, 1097 (1982); J. Aihara, *Pure Appl. Chem.*, **54**, 1115 (1982); K. Jug, *J. Org. Chem.*, **48**, 1344 (1983); W. Gründler, *Monatsch. Chem.*, **114**, 155 (1983).

Table 8.2. Energy Values for Reference Bond Types

Bond type	Hess-Schaad value (β)	Bond type	Moyano-Paniagua value (β)
$H_2C=CH$	2.000	$H_2C=CH-CH=$	2.2234
$HC=CH$	2.070	$H_2C=CH-C=$	2.2336
$H_2C=C$	2.000	$=CH-CH=CH-CH=$	2.5394
$HC=C$	2.108	$=CH-CH=CH-C=$	2.5244
$C=C$	2.172	$=C-CH=CH-C=$	2.4998
$HC-CH$	0.466	$H_2C=C-$	2.4320
$HC-C$	0.436	$-CH=CH-$	2.7524
$C-C$	0.436	$-C=C-$	2.9970

All these approaches agree that benzene and the structures that can be built up by fusing benzenoid rings together are strongly stabilized relative to the reference polyenes. The larger rings tend to have lower resonance energies per π electron than does benzene. This feature is in agreement with experimental trends in reactivity.[168] Schleyer and co-workers have applied some of the criteria of aromaticity to this series of compounds.[169] With application of the isodesmic equation below, the stabilization per electron was found to increase on going from benzene to naphthalene and then to remain approximately constant.

$$n = 0,1,2,3,4,5$$
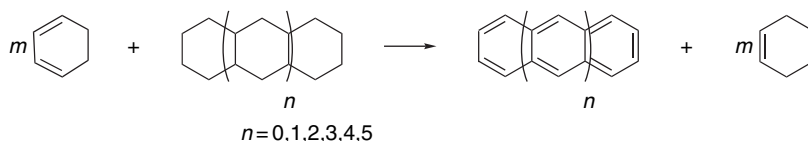
Another manifestation of aromatic stability is resistance to addition reactions. For example, the E_a and ΔH for cycloaddition with ethyne were calculated, and the results are shown as in Table 8.3. The internal rings have greater exothermicity and lower E_a.

one residual naphthalene ring

external ring

internal ring

two residual benzene rings
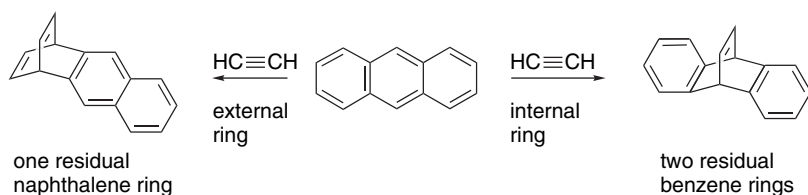
A similar trend is observed for the rates of Diels-Alder addition reactions of anthracene, naphthacene, and pentacene, in which three, four, and five rings, respectively, are linearly fused. The rate data are shown in Table 8.4. The same trend can be seen in the E_a and the gain in resonance energy when cycloreversion of the adducts **9–12** yields the aromatic compound, as shown in Scheme 8.3.

[168.] D. Biermann and W. Schmidt, *J. Am. Chem. Soc.*, **102**, 3163, 3173 (1980).
[169.] P. v. R. Schleyer, M. Manoharan, H. Jiao, and F. Stahl, *Org. Lett.*, **3**, 3643 (2001).

Table 8.3. Calculated Barriers and Reaction Energy for Cycloaddition of Ethyne with Polycyclic Hydrocarbons

Compound	E_a	ΔH
Benzene	43.8	6.1
Naphthalene	36.8	−8.7
Anthracene (external ring)	34.3	−13.9
Anthracene (center ring)	29.4	−26.2
Naphthacene (external ring)	33.3	−16.1
Naphthacene (internal ring)	26.8	−32.6
Pentacene (external ring)	32.7	−17.3
Pentacene (internal ring)	25.5	−35.4
Pentacene (center ring)	24.0	−39.5

Table 8.4. Rates of Diels-Alder Additions of Linear Polycyclic Aromatic Hydrocarbons[a]

	$k(M^{-1}s^{-1})$ in toluene at 80°C		
Dienophile	Anthracene	Naphthacene	Pentacene
Benzoquinone		44	181
Maleic anhydride	5	294	4710
N-Phenylmaleimide	10	673	19,280

a. V. D. Samuilov, V. G. Uryadov, L. F. Uryadova, and A. J. Konolova, *Zh. Org. Khim.* (Engl. Trans..), **21**, 1137 (1985).

Benzene rings can also be fused in angular fashion, as in phenanthrene, chrysene, and picene. These compounds, while quite reactive toward additions in the center ring, retain most of the REPE stabilization of benzene and naphthalene.[170]
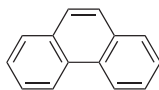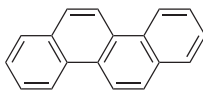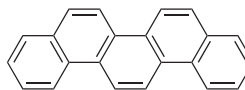
phenanthrene   chrysene   picene

Scheme 8.3. Correlation between E_a for Retro-Diels-Alder Reaction and Change in Resonance Stabilization of Polycyclic Hydrocarbons

	9 →	**10** →	**11** →	**12** →
	benzene	naphthalene	anthracene	naphthacene
E_a (kcal/mol)	16	20	29	31
ΔRE (kcal/mol)	40	30	17	11

170. K. B. Wiberg, *J. Org. Chem.*, **62**, 5720 (1997).

The NICS values for the linear polycyclic arenes show a pattern of increasing negativity (aromaticity) toward the center ring. In contrast, for phenanthrene, the center ring has the lowest NICS, consistent with the more localized nature of this ring.[171]
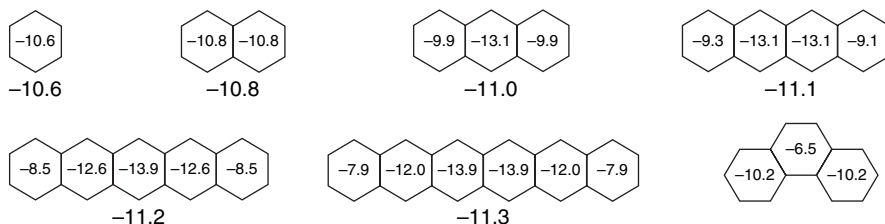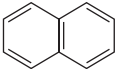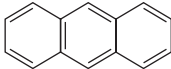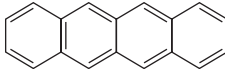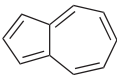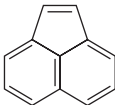
Average (beneath the structure) and individual ring (inside each ring) NICS values for polycyclic hydrocarbons. Except for phenanthrene the values are 1 Å above the ring.

The HOMO-LUMO gap decreases as the number of fused rings increases. The decreasing gap is reflected in the hardness values shown in Scheme 8.4, as assigned by Zhou and Parr.[172] The values for phenanthrene and acenaphthene, which have more localized double bonds, are 0.315 and 0.151, respectively. Similarly, the nonbenzenoid hydrocarbon azulene is calculated to be softer.

There is evidence that aromatic circuits can exist within a larger conjugated unit resulting in an aromatic segment in conjugation with a "localized" double bond. For example, in acenaphthene, the double bond in the five-membered ring is both structurally and chemically similar to a normal localized double bond. The resonance energy given in Scheme 8.2, 0.57ß, is slightly less than that for naphthalene (0.59ß). The additional double bond of acenaphthene has only a small effect on the stability of the conjugated system. The molecular structure determined at 80 K by neutron diffraction shows bond lengths for the aromatic portion that are quite similar to those

Scheme 8.4. HOMO-LUMO Gaps and Hardness for Polycyclic Hydrocarbons

HMO gap (β)	2.000	1.3360	0.8284	0.5900
Rel Hardness	0.482	0.264	0.151	0.088

HMO gap (β)	0.8775	0.9221	1.2104
Rel Hardness	0.253	0.206	0.315

[171.] P. v. R. Schleyer, M. Manoharan, H. Jiao, and F. Stahl, *Org. Lett.*, **3**, 3643 (2001).
[172.] Z. Zhou and R. G. Parr, *J. Am. Chem. Soc.*, **111**, 7371 (1989).

of naphthalene.[173] The double bond is somewhat longer than a normal double bond, but this may reflect the strain imposed on it by the naphthalene framework.

naphthalene   acenaphthene
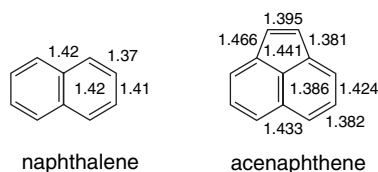
The predictions of relative stability by the various approaches diverge more widely when nonbenzenoid systems are considered. The simple Hückel method using total π delocalization energies relative to an isolated double-bond reference energy $(\alpha + \beta)$ fails. This approach predicts stabilization of the same order of magnitude for such unstable systems as pentalene and fulvalene as it does for much more stable aromatics. The HMO', RE, and SCF-MO methods, which use polyene reference energies, do much better. All show drastically reduced stabilization for such systems and, in fact, indicate destabilization of systems such as butalene and pentalene (Scheme 8.2).

It is of interest to consider at this point some of the specific molecules in Scheme 8.2 and compare their chemical properties with the calculated stabilization energies. Benzocyclobutadiene has been generated in a number of ways, including dehalogenation of dibromobenzocyclobutene.[174] Chemically, benzocyclobutadiene reacts as a polyene having a quinodimethane structure and is a reactive diene in Diels-Alder cycloadditions, dimerizing or polymerizing readily.[175]
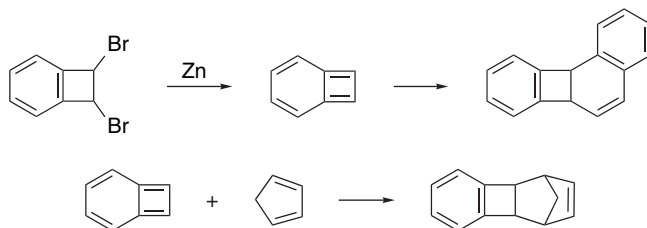
Ref. 176

Generation of benzocyclobutadiene by fluoride-induced elimination has permitted the NMR spectrum to be observed under flow conditions.[177] All the peaks are somewhat upfield of the aromatic region, suggesting polyene character.
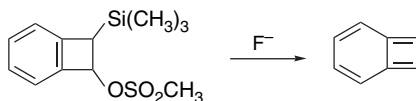
173. R. A. Wood, T. R. Welberry, and A. D. Rae, *J. Chem. Soc., Perkin Trans. 2*, 451 (1985).

174. M. P. Cava and D. R. Napier, *J. Am. Chem. Soc.*, **78**, 500 (1956); *J. Am. Chem. Soc.*, **79**, 1701 (1957).

175. (a) M. P. Cava and M. J. Mitchell, *Cyclobutadiene and Related Compounds*, Academic Press, New York, 1967, pp. 192–216; (b) M. K. Shepherd, *Cyclobutarenes: Chemistry of Benzocyclobutene, Biphenylene and Related Compounds*, Elsevier, New York, 1991; W. S. Trahanovsky and K. B. Arvidson, *J. Org. Chem.*, **61**, 9528 (1996); P. Gandhi, *J. Sci. Ind. Res.*, **41**, 495 (1982); M. P. Cava and D. R. Napier, *J. Am. Chem. Soc.*, **80**, 2255 (1958); M. P. Cava and M. J. Mitchell, *J. Am. Chem. Soc.*, **81**, 5409 (1959); A. K. Sadana, R. K. Saini, and W. E. Billups, *Chem. Rev.*, **103**, 1539 (2003).

176. M. P. Cava and M. J. Mitchell, *J. Am. Chem. Soc.*, **81**, 5409 (1959).

177. W. S. Trahanovsky and D. R. Fischer, *J. Am. Chem. Soc.*, **112**, 4971 (1990).

The ring current in benzocyclobutadiene has been analyzed in detail.[178] The main ring current is associated with the four-membered ring and is paramagnetic. This is consistent with the calculated NICS values, which are −2.5 for the six-membered ring and 22.5 for the four-membered ring.[179] The fusion of the cyclobutadiene ring to benzene greatly diminishes the aromatic character of the benzenoid ring. The implication of a nonaromatic structure is that the combination of ring strain and the antiaromaticity associated with the four-membered ring results in a localized system.[180]

Azulene is one of the few nonbenzenoid hydrocarbons that appear to have appreciable aromatic stabilization. There is some divergence on this point between the SCF-MO and HMO' results in Scheme 8.2. The latter estimates a resonance energy about half that for the isomeric naphthalene, whereas the SCF-MO method assigns a resonance energy that is only about one-seventh that of naphthalene. Naphthalene is thermodynamically more stable than azulene by about 38.5 kcal/mol. Molecular mechanics calculations attribute about 12.5 kcal/mol of the difference to strain and about 26 kcal/mol to greater resonance stabilization of naphthalene.[181] Based on heats of hydrogenation, the stabilization energy of azulene is about 16 kcal/mol.[182] The parent hydrocarbon and many of its derivatives are well-characterized compounds with considerable stability. The structure of azulene has been determined by both X-ray crystallography and electron-diffraction measurements.[183] The peripheral bond lengths are in the aromatic range and show no regular alternation. The bond shared by the two rings is significantly longer, indicating that it has predominantly single-bond character, which indicates that the conjugated system more closely resembles [10]annulene than naphthalene. Theoretical calculations indicate that the molecule has C_{2v} symmetry, suggesting delocalization of the π electrons.[184]

azulene   X-ray bond lengths   electron diffraction bond lengths
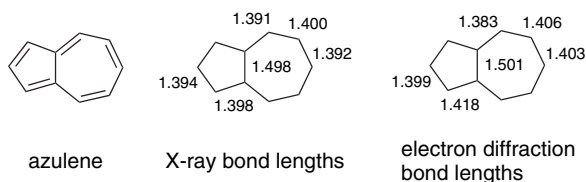
An interesting structural question involves the contribution of a dipolar structure that pictures the molecule as the fusion of a cyclopentadienide anion and a cycloheptatrienyl cation.

178. A. Soncini, R. W. A. Havenith, P. W. Fowler, L. W. Jenneskens, and E. Steiner, *J. Org. Chem.*, **67**, 4753 (2002); R. W. A. Havenith, F. Lugli, P. W. Fowler, and E. Steiner, *J. Phys. Chem. A*, **106**, 5703 (2002).
179. P. v. R. Shleyer, C. Maerker, A. Dransfeld, H. Jiao, and N. J. R. van Eikema Hommes, *J. Am. Chem. Soc.*, **118**, 6317 (1996).
180. P. B. Karadakov, J. Gerratt, D. L. Cooper, M. Raimondi, and M. Sironi, *Int. J. Quantum Chem.*, **60**, 545 (1996); M. O. Jensen, T. Thorsteinsson, and A. E. Hansen, *Intl. J. Quantum Chem.*, **90**, 616 (2002).
181. N. L. Allinger and Y. H. Yu, *Pure Appl. Chem.*, **55**, 191 (1983).
182. W. R. Roth, M. Boehm, H. W. Lennartz, and E. Vogel, *Angew. Chem. Int. Ed. Engl.*, **22**, 1007 (1983).
183. A. W. Hanson, *Acta Crystallogr.*, **19**, 19 (1965); O. Bastiansen and J. L. Derissen, *Acta Chem. Scand.*, **20**, 1319 (1966).
184. (a) C. Glidewell and D. Lloyd, *Tetrahedron*, **40**, 4455 (1984); (b) R. C. Haddon and K. Raghavachari, *J. Am. Chem. Soc.*, **104**, 3516 (1982); (c) S. Grimme, *Chem. Phys. Lett.*, **201**, 67 (1993); (d) S. J. Mole, X. Zhou, J. G. Wardeska, and R. Liu, *Spectrochim. Acta A*, **52**, 1211 (1996); (e) B.-C. Wang, Y.-S. Lin, J.-C. Chang, and P.-Y. Wang, *Can. J. Chem.*, **78**, 224 (2000); (f) I. Bandyopadhyay, *Theochem*, **618**, 59 (2002).
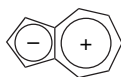
Azulene does have an appreciable dipole moment (0.8 D).[185] B3LYP/6-31G* and MP2/6-31G* computations calculate the dipole moment as about 1.0 D.[184c,d] The essentially single-bond nature of the shared bond indicates, however, that the conjugation is principally around the periphery of the molecule.

The significant resonance stabilization of azulene can be contrasted with pentalene and heptalene, both of which are indicated to be destabilized relative to a reference polyene.

pentalene   heptalene
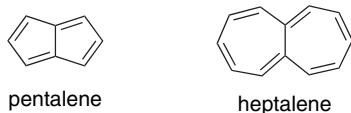
Preparation of pentalene is followed by immediate dimerization.[186] Low-temperature photolysis produces a new species believed to be pentalene, but the compound reverts to dimer at −100°C. The matrix-isolated monomer has been characterized spectroscopically,[187] and the results are in accord with the predicted lack of stabilization.[188]
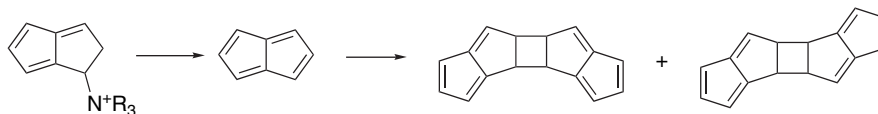
Heptalene readily polymerizes and is sensitive to oxygen. The NMR spectrum does not indicate the presence of an aromatic ring current. The conjugate acid of heptalene, however, is very stable (even at pH 7 in aqueous solution), reflecting the stability of the cation, which is a substituted tropylium ion.[189]
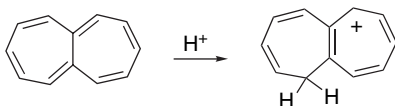
Another structure with a ten electron conjugated system is bicyclo[6.2.0]deca-1,3,5,7,9-pentaene. The crystal structure of the 9,10-diphenyl derivative shows the conjugated system to be nearly planar,[190] but there is significant bond alternation.
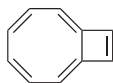
[185.] H. J. Tobler, A. Bauder, and H. H. Günthard, *J. Mol. Spectrosc.*, **18**, 239 (1965); G. W. Wheland and D. E. Mann, *J. Chem. Phys.*, **17**, 264 (1949).
[186.] K. Hafner, R. Donges, E. Goedecke, and R. Kaiser, *Angew. Chem. Int. Ed. Engl.*, **12**, 337 (1973); S. You and M. Neuenschwander, *Chimia*, **50**, 24 (1996).
[187.] T. Bally, S. Chai, M. Neuenschwander, and Z. Zhu, *J. Am. Chem. Soc.*, **119**, 1869 (1997).
[188.] T. K. Zywietz, H. Jiao, P. v. R. Schleyer, and A. de Meijere, *J. Org. Chem.*, **63**, 3417 (1998).
[189.] H. J. Dauben, Jr., and D. J. Bertelli, *J. Am. Chem. Soc.*, **83**, 4657, 4659 (1961).
[190.] C. Kabuto and M. Oda, *Tetrahedron Lett.*, 103 (1980).

The bond at the ring fusion is quite long. A molecular mechanics calculation on this molecule, which includes an SCF-MO treatment of the planar conjugated system, concluded that the molecule is slightly destabilized (4 kcal/mol) relative to a polyene reference.[191] HF/STO-3G calculations found a small stabilization.[192] An experimental determination of ΔH_{H_2} also suggests a small (3.7 kcal/mol) stabilization.[193]

The tricyclic fused systems known as *s*-indacene and *as*-indacene have also been of interest in assessing the range of aromaticity. *s*-Indacene derivatives have bond lengths varying from 1.39 to 1.44 Å in the crystal structure.[194] MO and DFT calculations vary in predicting the relative energy of localized and delocalized structures.[195] B3LYP/6-31G* calculations place the structures within 0.1 kcal/mol of one another.[196] An aromatic stabilization of 10.8 kcal/mol is calculated based on the following isodesmic reaction, which is much less than for anthracene.[197] The NICS values for both rings are positive and indicate a paramagnetic ring current.

ASE = 10.8 kcal/mol
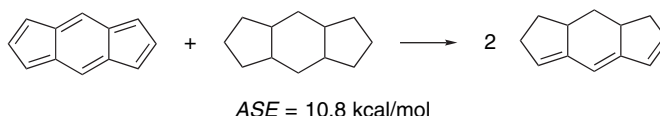
The possibility of extra stabilization in systems that have conjugated components exocyclic to the ring has also been examined. Such substituents complete conjugated rings but are not part of the cyclic system. Some representative structures are shown in Scheme 8.5.

Cyclopropenes and cyclopentadienes with exocyclic double bonds provide the possibility of dipolar resonance structures that suggest aromatic character in the cyclic structure.

triafulvene   fulvene
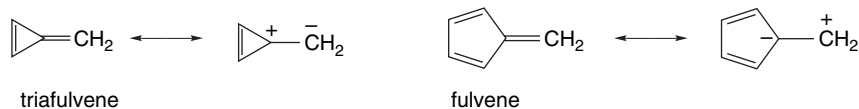
For methylenecyclopropene, a microwave structure determination has established bond lengths that show the strong alternation anticipated for a localized structure.[198] The molecule does have a significant (1.90 D) dipole moment, implying a contribution from the dipolar resonance structure. The net stabilization calculated at the MP/6-31G* level is small and comparable to the stabilization of 1,3-butadiene. The molecular geometry

[191] N. L. Allinger and Y. H. Yuh, *Pure Appl. Chem.*, **55**, 191 (1983).

[192] D. Cremer, T. Schmidt, and C. W. Bock, *J. Org. Chem.*, **50**, 2684 (1985).

[193] W. Roth, H. -W. Lennartz, E.Vogel, M. Leiendecker, and M. Oda, *Chem. Ber.*, **119**, 837 (1986).

[194] K. Hafner, B. Stowasser, H. -P. Krimmer, S. Fischer, M. C. Böhm, and H. J. Lindner, *Angew. Chem. Intl. Ed. Engl.*, **25**, 6201 (1986); J. D. Dunitz, C. Kruger, H. Imgartinger, E. F. Maverick, Y. Wang, and M. Nixdorf, *Angew. Chem. Intl. Ed. Engl.*, **27**, 387 (1988).
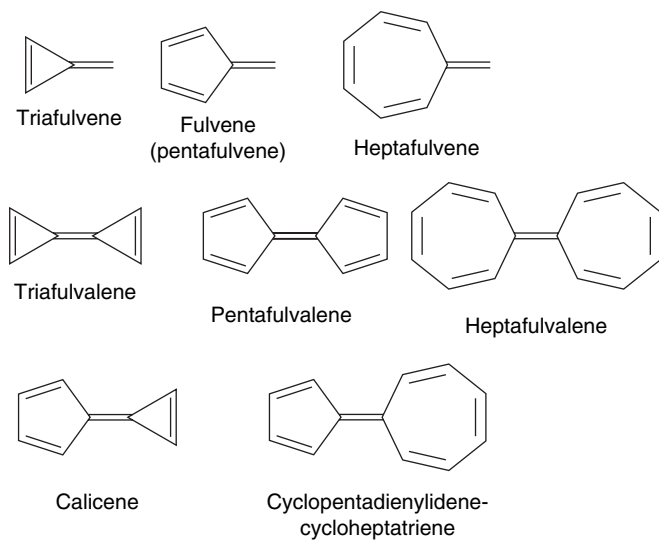
[195] C. Gellini, G. Cardini, P. R. Salvi, G. Marconi, and K. Hafner, *J. Phys. Chem.*, **97**, 1286 (1993); R. H. Hertwig, M. C. Holthausen, W. Koch, and Z. B. Maksic, *Angew. Chem. Intl. Ed. Engl.*, **33**, 1192 (1994); R. H. Hertwidg, M. C. Holthausen, and W. Koch, *Intl. J. Quantum Chem.*, **54**, 147 (1995).

[196] M. Nendel, B. Goldfuss, B. Beno, K. N. Houk, K. Hafner, and H.-J. Lindner, *Pure Appl. Chem.*, **71**, 221 (1999).

[197] M. Nendel, B. Goldfuss, K. N. Houk, and K. Hafner, *Theochem*, **461-2**, 23 (1999).

[198] T. D. Norden, S. W. Staley, W. H. Taylor, and M. D. Harmony, *J. Am. Chem. Soc.*, **108**, 7912 (1986).

Scheme 8.5. Completely Conjugated Hydrocarbons Incorporating Exocyclic Double Bonds

Triafulvene   Fulvene (pentafulvene)   Heptafulvene

Triafulvalene   Pentafulvalene   Heptafulvalene

Calicene   Cyclopentadienylidene-cycloheptatriene

of dimethylfulvene has been examined by electron diffraction methods. Strong bond length alternation indicative of a localized structure was found.[199]

The fulvalene systems are not predicted to be aromatic by any of the theoretical estimates of stability. Even simple resonance considerations would suggest polyene behavior, since only dipolar resonance structures can be drawn in addition to the single nonpolar structure.

triafulvalene   pentafulvalene   heptafulvalene
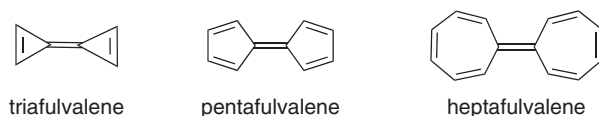
Triafulvalene (cyclopropenylidenecyclopropene) has not been isolated. A substantial number of pentafulvalene derivatives have been prepared.[200] The chemical properties of these molecules are those of reactive polyenes. The NMR spectrum of pentafulvalene is characteristic of a localized system.[201] Heptafulvalene (cycloheptatrienylidenecycloheptatriene) is a well-characterized compound with the properties expected for a polyene.[202]

[199.] J. F. Chiang and S. H. Bauer, *J. Am. Chem. Soc.*, **92**, 261 (1970).

[200.] E. D. Bergmann, *Chem. Rev.*, **68**, 41 (1968).

[201.] E. Escher, P. Bönzli, A. Otter, and M. Neuenschwander, *Mag. Reson. Chem.*, **24**, 350 (1986).

[202.] T. Nozoe and I. Murata, *Int. Rev. Sci.*, *Org. Chem. Ser. Two*, **3**, 197 (1976).

Because the five-membered ring is a substituted cyclopentadienide anion in some dipolar resonance structures, it might be expected that exocyclic groups that could strongly stabilize a positive charge might lead to a larger contribution from dipolar structures and enhanced stability. Structures **13** and **14** are cases in which a large dipolar contribution would be feasible.

13   **14**
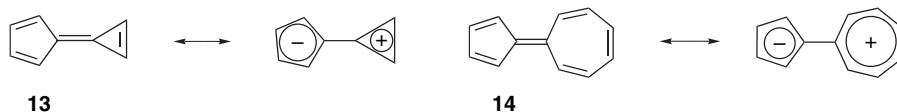
The stability of such dipolar systems depends on the balance between the increase in energy required to separate unlike charges and the aromaticity associated with Hückel $4n + 2$ systems. The parent compound, tripentafulvalene, is unknown, but BLYP/6-31G* and MP2/6-31G* calculations suggest some delocalization and a substantial dipole moment.[203] Phenyl-substituted analogs are known, and the large measured dipole moments suggest considerable charge separation.

μ = 6.3 D
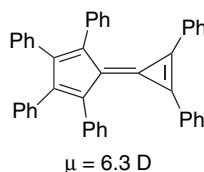
Ref. 204

Some alkyl derivatives have been prepared. Their chemical behavior is that of highly reactive polyenes. One interesting property does appear in the NMR spectra, which reveal a reduced barrier to rotation about the double bond between the two rings.[205] This property suggests that rotation about this bond takes place easily through a TS in which the two charged aromatic rings are twisted out of conjugation.
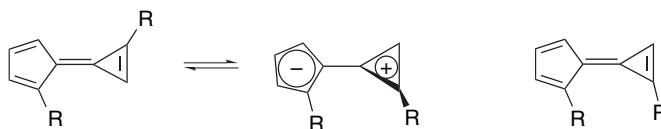
MO calculations (HF/STO-3G and HF/3-21G) indicate a rotational barrier that is substantially reduced relative to the corresponding barrier in ethene. The TS for the rotation is calculated to have a charge separation of the type suggested by the dipolar resonance structure.[206]

Agranat, Radom, and co-workers surveyed the fulvene and fulvalene combinations including three-, five-, and seven-membered rings. Structures and energies were calculated at the BLYP/6-31G* and MP2/6-31G* levels.[203] A large destabilization was found for triafulvalene on the basis of homodesmotic reactions. The potentially

203. A. P. Scott, I. Agranat, P. U. Biedermann, N. V. Riggs, and L. Radom, *J. Org. Chem.*, **62**, 2026 (1997).

204. E. D. Bergmann and I. Agranat, *J. Chem. Soc. Chem. Commun.*, 512 (1965).

205. A. S. Kende, P. T. Izzo, and W. Fulmer, *Tetrahedron Lett.*, 3697 (1966); H. Prinzbach, *Pure Appl. Chem.*, **28**, 281 (1971).

206. B. A. Hess, Jr., L. J. Schaad, C. S. Ewig, and P. Carsky, *J. Comput. Chem.*, **4**, 53 (1982).

favorable three-five and five-seven combinations showed somewhat larger stabilizations than the five-five and seven-seven combinations.

(structure)	− 47.8	(structure)	+ 11.2
(structure)	+ 33.9	(structure)	+ 27.7
(structure)	− 3.4	(structure)	+ 17.6
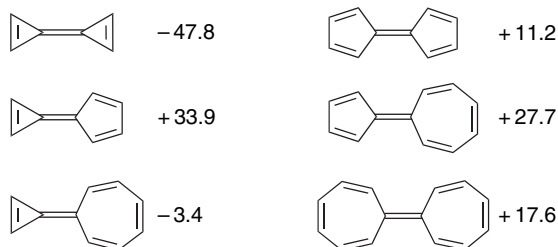
The hydrocarbon phenalene is the precursor of a highly stabilized anion and cation. The HMO diagram is shown in Figure 8.10. The single orbital at the nonbonding level is the LUMO in the cation and the HOMO in the anion. The stabilization energy calculated is the same for both and is 0.41ß by the HMO' comparison.[207] The pK for conversion of phenalene to its anion is 19.[208] The cation is estimated to have a pK_{R+} of about 0–2.[209] Several methods for generating the phenalenyl cation have been developed.[210] Since the center carbon is part of the conjugated system, the Hückel rule, which applies only to *monocyclic* conjugated systems, cannot be applied to just the peripheral conjugation. The nature of the phenalenyl system is considered further in Problem 8.12.

(reaction scheme: cation ← −H⁻ — phenalene — +e⁻ → anion)

phenalene
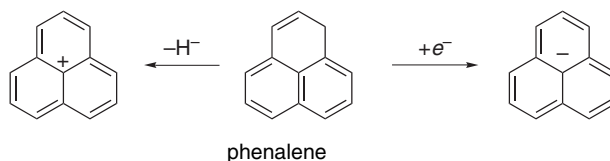
The general conclusion is that the HMO′, RE, and SCF methods based on comparison with conjugated polyenes make reasonably accurate predictions about the stabilization in conjugated molecules. The stabilization is general for benzenoid compounds, but quite restricted in nonbenzenoid systems. Since the HMO′, method of estimating stability is based on the ideas of HMO theory, its success vindicates the ability of this very simplified MO approach to provide insight into the structural nature of the annulenes and other conjugated polyenes. Of course, more sophisticated MO methods are now accessible and can be applied for more detailed analyses of the structures of these molecules.

$$\alpha$$
$$\alpha + \beta$$
$$\alpha + 1.73\beta$$
$$\alpha + 2.45\beta$$
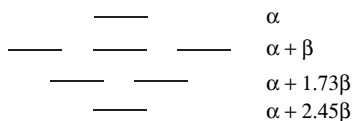
Fig. 8.10. Hückel molecular orbitals for phenalenyl.

[207.] J. Aihara, *Bull. Chem. Soc. Japan*, **51**, 3540 (1978); P. Ilic and N. Trinjastic, *J. Org. Chem.*, **45**, 1738 (1980).
[208.] A. Streitwieser, Jr., J. M. Word, F. Guibe, and J. S. Wright, *J. Org. Chem.*, **46**, 2588 (1981); R. A. Cox and R. Stewart, *J. Am. Chem. Soc.*, **98**, 488 (1976).
[209.] D. Menche, H. Strauss, and E. Heilbronner, *Helv. Chim. Acta*, **41**, 57 (1958).
[210.] I. Murata, in *Topics in Nonbenzenoid Aromatic Chemistry*, T. Nozoe, R. Breslow, K. Hafner, S. Ito, and I. Murata, ed., Hirokawa, Tokyo, 1976, pp. 159–190.

8.6. Heteroaromatic Systems

Certain structural units containing heteroatoms can be inserted into aromatic systems in such a way that the system remains conjugated and isoelectronic with the original hydrocarbon. The most common examples are $-CH=N-$ and $-N=N-$ double bonds and divalent sp^2 $-O-$, $-S-$, and $-NR-$ units. Each of these structural fragments can replace $-CH=CH-$ in an aromatic ring and contribute two π electrons.[211] These compounds are called *heteroaromatic* to recognize both their heterocyclic and aromatic nature. Scheme 8.6 gives some of the common structures that are isoelectronic with benzene and naphthalene.

Various approaches have been taken to estimate the aromaticity of these compounds. The Hess-Schaad HMO′, values are available,[212] as are SCF comparisons with polyene models.[213] Generally speaking, the various approaches suggest that the aromatic stabilization of pyridine is similar to that of benzene. This is in agreement with thermochemical estimates of the pyridine stabilization energy.[214] Typically, the five-membered compounds are found to be somewhat less stabilized than benzene with resonance energies in the range of 0.5 to 0.75 of that for benzene.[215] Theoretical calculations at the MP2/6-31G* and B3LYP/6-31G** have provided aromatic stabilization energies (ASE; see p. 717).
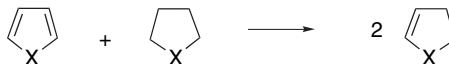
The ASE values correlate with magnetic susceptibility for the five-membered heteroaromatic compounds.[216] Magnetic and polarizability criteria put the order of aromaticity as thiophene > pyrrole > furan.[215a,c] The other criteria of aromaticity discussed in Section 8.2 are also applicable to heterocyclic compounds. HOMO-LUMO gaps[217] and Fukui functions[218] (see Topic 1.5) have been calculated for compounds such as indole, benzofuran, and benzothiophene and are in accord with the known reactivity patterns of these heterocycles.

Additional heteroaromatic structures can be built up by fusing benzene rings to the aromatic heterocyclic rings or by fusing heterocyclic rings together. Examples of the former type are included in Scheme 8.6. When benzene rings are fused to the heterocyclic five-membered rings, the structures from fusion at the 2,3-positions are much more stable than those from fusion at the 3,4-positions. The π-electron system in the 3,4-fused compounds is more similar to a peripheral 10 π-electron system than

211. B. Ya. Simkin, V. I. Minkin, and M. N. Glukhovtsev, *Adv. Heterocycl. Chem.*, **56**, 303 (1993).

212. B. A. Hess, L. S. Schaad, and C. W. Holyoke, *Tetrahedron*, **31,** 295 (1975); B. A. Hess and L. S. Schaad, *J. Am. Chem. Soc.*, **95**, 3907 (1973).

213. M. J. S. Dewar, A. J. Harget, N. Trinjastic, and S. D. Worley, *Tetrahedron*, **28**, 4505 (1970).

214. K. B. Wiberg, D. Nakaji, and K. M. Morgan, *J. Am. Chem. Soc.*, **115**, 3527 (1993).

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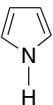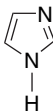
216. P. v. R. Schleyer, P. K. Freeman, H. Jiao, and B. Goldfuss, *Angew. Chem. Int. Ed. Engl.*, **34**, 337 (1995); M. K. Cyranski, P. v. R. Schleyer, T. M. Krygowski, H. Jiao, and G. Hohlneicher, *Tetrahedron*, **59**, 1657 (2003).

217. B. S. Jursic, *J. Heterocycl. Chem.*, **33**, 1079 (1996); B. S. Jursic, *Theochem*, **468**, 171 (1999).
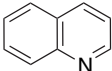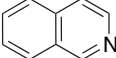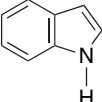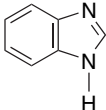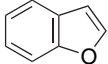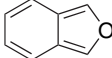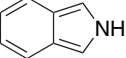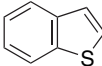
218. R. Salcedo, A. Martinez, and L. E. Sansores, *Tetrahedron*, **57**, 8759 (2001); A. Martinewz, M.-V. Vazquez, J. L. Carreon-Macedo, L. E. Sansores, and R. Salcedo, *Tetrahedron*, **59**, 6415 (2003).

Scheme 8.6. Stabilization Energy and Index of Aromaticity for Heteroaromatic Compounds Isoelectronic with Benzene and Naphthalene

A. Structures isoelectronic with benzene

	Pyridine	Pyrimidine	Pyrazine	Pyridazine	s-Triazine
SE	43.3	40.6	40.9	32.7	44.9
HMO'	0.35	0.30	0.29		
SCF-MO	20.9	20.2	14.6		
AM1	25.6	25.0	24.6	22.6	
IA	86	84	89	79	100

	Furan	Pyrrole	Thiophene	Imidazole	Thiazole
SE	27.2	40.4	43.0	48.3	42.0
HMO'			0.19	15.4	
SCF-MO	1.6	8.5			
AM1	12.1	22.5	16.5		
IA	53	90	81.5	79	79

B. Structures isolelectronic with naphthalene

	Quinoline	Isoquinoline	Indole	Benzimidazole
SE	81.0	81.0	73.8	78.9
HMO'	0.51	0.52		30.9
SCF-MO	32.9			
IA	134	133	146	148

|	Benzofuran	Isobenzofuran	Isoindole	Benzothiophene
SE	55.4			
HMO'				0.44
SCF-MO	20.3			
IA	94			

SE: Thermochemical stabilization in kcal/mol based on the difference between ΔH_f and summation of standard bond energies. Benzene = 45.8 kcal/mol. C. W. Bird, *Tetrahedron,* **48**, 335 (1992); *Tetrahedron*, **52**, 9945 (1996).

HMO′: HMO stabilization in β relative to localized bond model. Benzene = 0.39; B. A. Hess, Jr., L.J. Schaad, and C. W. Holyoke, *J. Org. Chem.*, **31**, 295 (1975); B. A. Hess, Jr, and L. J. Schaad, *J. Am. Chem. Soc.*, **95**, 3907 (1973).

SCF-MO: Difference in total energy in kcal/mol relative to polyene model; Benzene = 20 kcal/mol. M. J. S. Dewar, A. J. Harget, and N. Trinajstic, *J. Am. Chem. Soc.*, **91**, 6321 (1969).

AM1: Stabilization in kcal/mol relative to localized model using AM1 semiempirical calculations; M. J. S. Dewar and A. J. Holder, *Heterocycles*, **28**, 1135 (1989).

IA: Index of aromaticity based on bond length variation. Benzene = 100.

to the 10 electron system for naphthalene. As a result these compounds have a strong tendency to undergo reactions that restore benzene conjugation in the carbocyclic ring. The isobenzofuran structure **15** is known to be an exceptionally reactive diene, for example. Isoindole, **16**, readily tautomerizes to the benzenoid imine **17**.
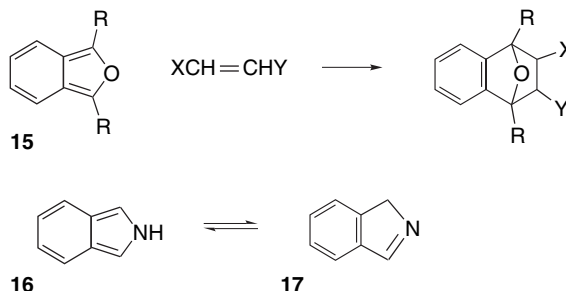

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E. Clar, *Polycyclic Hydrocarbons*, Academic Press, New York, 1964.

P. J. Garratt, *Aromaticity*, Wiley, New York, 1986.

I. Gutman and S. J. Cyvin, *Introduction to the Theory of Benzenoid Hydrocarbons*, Springer-Verlag, Berlin, 1989.

D. Lloyd, *Nonbenzenoid Conjugated Carbocyclic Compounds*, Elsevier, Amsterdam, 1984.

V. I. Minkin, M. N. Glukhovtsev and B. Y. Simkin, *Aromaticity and Anti-aromaticity*, Wiley, New York, 1994.

M. Sainsbury, *Aromatic Chemistry*, Oxford University Press, Oxford, 1992.

Problems

(*References for these problems will be found on page 1163*.)

8.1. The reaction of 1,2-diphenylcyclobutadiene (generated in situ by oxidation of its iron tricarbonyl complex) with *p*-benzoquinone yields adduct **1-A** as the exclusive product. A completely analogous structure is obtained using maleimide as the dienophile. However, with the more reactive dienophiles tetra-cyanoethylene and dicyanomalemide, two isomeric adducts of type **1-B** and **1-C** are found in a 1:7 ratio in each case. Discuss these results and explain how they relate to the issue of a square versus a rectangular structure for the cyclobutadiene ring.
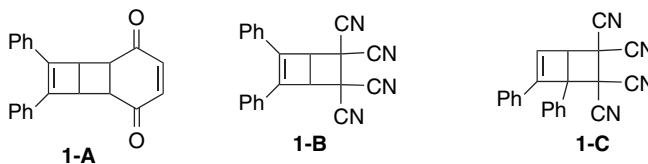

8.2. A single resonance structures is shown below for each of several molecules. Consider other resonance structures and identify those that would be expected to make a major stabilizing contribution to the molecule in question.

(a) (b) (c) Ph (d)
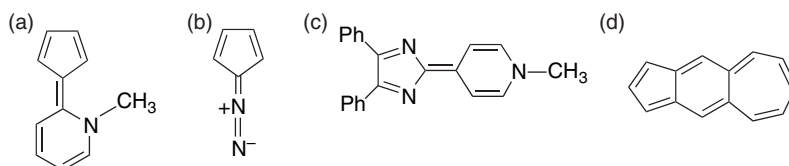
8.3. a. A synthesis of tropone (cycloheptatrienone) entails treating 1-methoxy-1,3,5-cycloheptatriene with bromine. A salt is produced that yields tropone on treatment with aqueous $NaHCO_3$. What is a likely structure for the salt? Write a mechanism for its formation and for the formation of tropone on hydrolysis.

  b. The optically active dichlorophenylcyclobutenone **3-A** undergoes racemization in acetic acid at 100°C. Suggest an experiment to determine if the enol (a hydroxycyclobutadiene) is an intermediate.
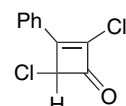
3-A

8.4. Predict whether or not the following structures would show strong delocalization and stabilization (aromatic), weak stabilization by conjugation (nonaromatic), or strong destabilization (antiaromatic) relative to acyclic model structures. Explain the basis for your prediction.

(a) (b) (c)

(d) (e) (f)

(g) (h) (i)
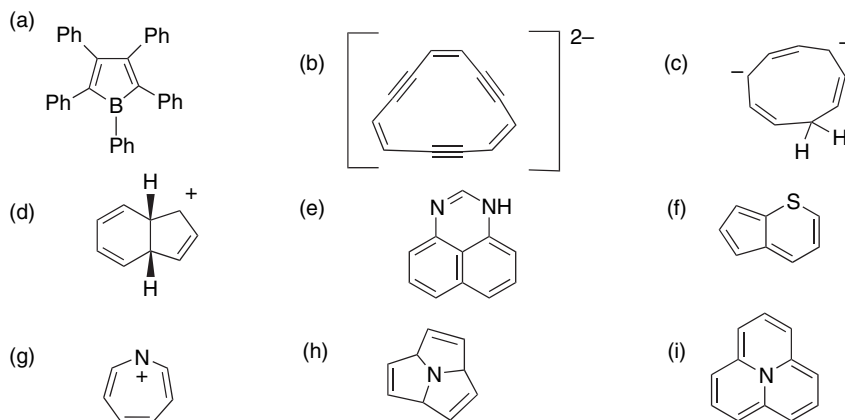
8.5. Bicyclo[6.2.0]deca-2,4,6,8,10-pentaene has been synthesized, and a number of MO and MM calculations have been performed to assess its aromaticity or antiaromaticity. Consider the structure and discuss the points below.

  a. What aspects of the structure suggest that antiaromaticity might be observed?
 b. What aspects of the structure suggest that aromaticity might be observed?

c. What are some of the experimental and computational criteria that could be applied to assess aromaticity or antiaromaticity? Cite at least three such probes and indicate the nature of the observation and interpretation.

8.6. Using the empirically chosen energy equivalents for bond types given on p. 748 and a standard compilation of HMO calculations, determine the resonance energies of the following molecules by the Hess-Schaad procedure (p. 747). Do you find any discrepancies between the predicted and observed properties, as described in Section 8.5?

(a) (b) (c) (d) (e)
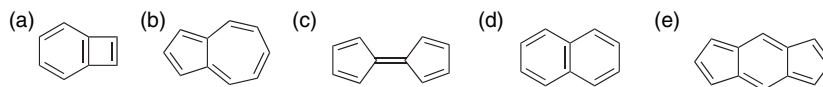
8.7. The completely conjugated cyclic polyenones have attracted considerable interest. Consider the following aspects of their properties:

a. The relative basicity of carbonyl oxygens can be measured by studying the strength of hydrogen bonding with a hydrogen donor such as phenol. The K_{eq} for 1:1 complexation of the following substituted cyclenones was determined. What conclusions do you draw from these data?

K_{eq} 6.2   31.2   83.2   117
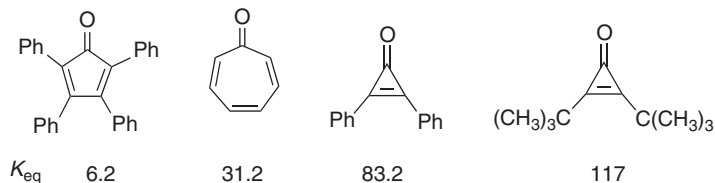
b. There have been extensive physical and chemical studies on cyclopropenone, cyclopentadienone, and cycloheptatrienone (tropone). The results of these studies can be briefly summarized as follows: (a) cyclopropenone appears to be stabilized by 20 ± 5 kcal/mol, relative to localized model structures; (b) cyclopentadienone is a kinetically unstable molecule; (c) tropone is estimated to be stabilized by less than 10 kcal/mol, relative to localized models. It is nonplanar and rather reactive. Rationalize these results in terms of MO concepts.

8.8. The isodesmic reaction series shown below has been used to compare the stabilities of the cyclopolyene ketenes. The total energies (HF/6-31G*) are given in hartrees. Calculate the stabilization found for each cyclopolyene ketene for $n = 1-3$. Account for the differences in stabilization and compare the results of these exocyclic ketenes to the corresponding cyclopolyenones (Problem 8.7).

$CH_3CH=CH_2$ $CH_3CH=C=O$
−117.0715   −190.7592   −227.3303   −304.3387   −381.2154   −153.6698   −230.6444   −307.5368
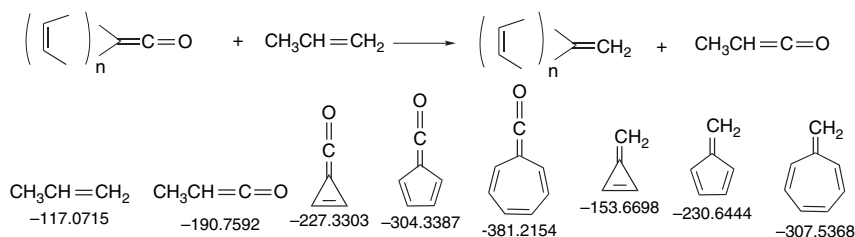
8.9. One criterion of aromaticity is the diamagnetic ring current, which is indicated by a substantial chemical shift difference between hydrogens in the plane of a conjugated system and those above or below the plane. The chemical shifts of two isomeric hydrocarbons are given below. In qualitative terms, which compound appears to be more aromatic? (Because the chemical shift owing to ring current depends on the detailed geometry, a quantitative calculation would be necessary to confirm the correctness of the qualitative assessment.) Does HMO theory predict a difference in the aromaticity of these two compounds?

external hydrogens
at 9.3 - 9.5 pppm

external hydrogens
at 7.2 - 7.9 ppm
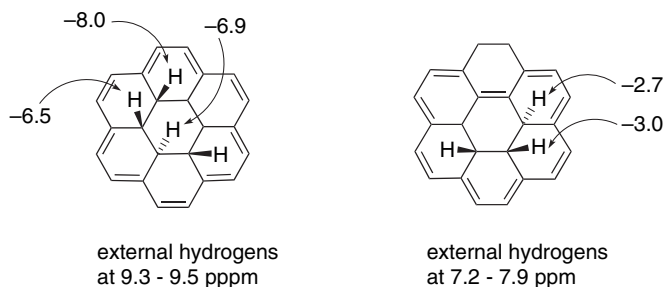
8.10. Offer an explanation for the following observations:

a. Hydrocarbon **10-A** $(\mathrm{p}K \approx 14)$ is considerably more acidic than **10-B** $(\mathrm{p}K \approx 22)$.
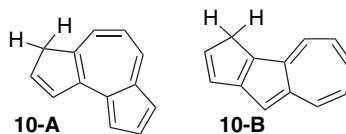

b. Hydrocarbon **10-C** has an unusually small separation of its oxidation and reduction potentials, as established by electrochemical measurements. It is both easily reduced and easily oxidized. Both mono- and dications and mono- and dianions can be readily formed.
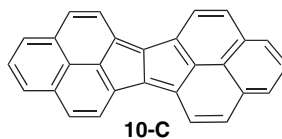

c. The barrier for rotation about the marked bond in **10-D** is only about 14 kcal/mol.
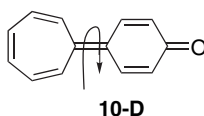
d. The hydrocarbon **10-E** is easily reduced to a dianion. The ^{1}HNMR spectrum of the dianion shows an average downfield shift relative to the hydrocarbon. The central carbon shows a large upfield shift in the ^{13}C-NMR spectrum.
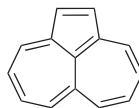

10-E

8.11. The HMOs for acenaphthene are shown below. The atomic coefficients for the orbital that is the LUMO in the neutral compound and the HOMO in the dianion are given at the right.
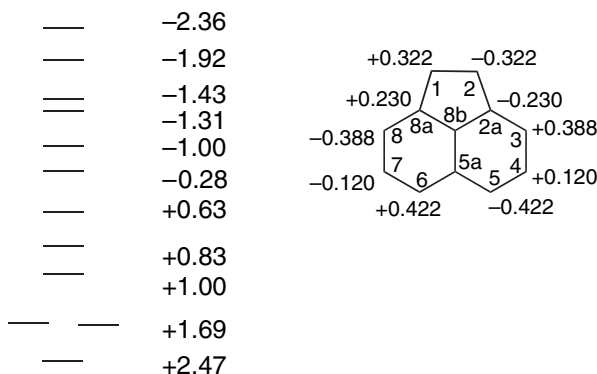

Comment on the aromaticity, antiaromaticity, or nonaromaticity of acenaphthene and its dianion on the basis of the following physical measurements:

a. The bond lengths of acenaphthene are given below. Compare them with the bond lengths for naphthalene given on p. 18. What conclusions can you draw about the aromaticity of acenaphthene?
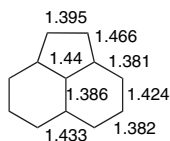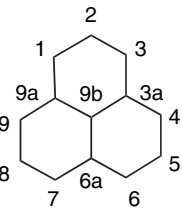

b. Both X-ray crystallography and NMR data indicate that the C(1)−C(2) bond lengthens significantly in the dianion, as indicated below (X-ray data). There is also a different pattern of bond length alternation. What conclusions can you draw about the aromaticity of the acenaphthene dianion?
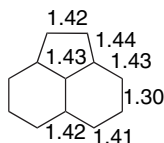
c. The ^{1}H- and ^{13}C-NMR shifts for acenaphthene and its dianion (Na${}^+$ counterion) are given below. What conclusions about charge density and aromaticity can be drawn from these data?

		1,2	3,8	4,7	5,6	2a,8a	5a	8b
^{1}H	Neutral	7.04	7.65	7.50	7.78			
	Dianion	4.49	4.46	5.04	3.34			
^{13}C	Neutral	129.9	124.7	128.3	127.8	140.7	129.1	129.3
	Dianion	86.1	97.0	126.8	82.6	123.4	149.3	137.7

8.12. The ^{1}H-NMR and ^{13}C-NMR spectra of both the anion and cation derived from phenalene have been observed. The HMO pattern for phenalene is given below.

			HMO coefficients					
atom	Energy(β)							
	2.44949	1.73205	1.73205	1.00000	1.0000	1.0000	0.0000
1	0.22361	0.35355	0.20412	−0.00473	−0.35355	−0.27382	−0.40825
2	0.18257	0.	0.00000	−0.00947	−0.00000	−0.54764	−0.20000
9a	0.36515	0.20412	0.35355	−0.00473	−0.35355	0.27382	0.00000
9b	0.44721	0.00000	0.00000	−0.40811	0.00000	0.37215	0.00000
9	0.22361	−0.00000	0.40825	0.41134	0.00000	0.17549	0.40825
8	0.18257	−0.20412	0.035355	040661	0.35355	−0.09833	0.00000
7	0.22361	−0.35355	0.20412	−0.00473	0.35355	−0.27382	−0.40825
6a	0.36515	−0.40825	0.00000	−0.41434	0.00000	−0.17549	−0.00000

The chemical shifts observed for the cation and anion are given below.

	^{1}H-NMR		^{13}C-NMR			
	C(1)	C(2)	C(1)	C(2)	C(9b)	C(3a)
[Cation]	9.38	8.55	155.5	133.7	123.7	133.7
[Anion]	5.36	6.10	103.4	128.0	139.6	145.0

What conclusions can be drawn about electron distribution in the cation and anion from the NMR data and how does it relate to the HMO pattern?

8.13. The ^{13}C-NMR spectrum of octalene (**13-A,13-B**, or **13-C**) is temperature dependent. At −150°C, there are signals for 14 different carbons. At −100°C, these collapse to seven different signals. Above 80°C, all but one of the remaining signals become broad. Although not attained experimentally, because of decomposition, it would be expected that only four different signals would be obtained at still higher temperature. (1) Show that these data rule out structures **13-A** and **13-B** for the room temperature structure of octalene, and favor structure **13-C**. (2) What is the nature of the dynamic process that converts the 14-line spectrum

to a 7-line spectrum? (3) What would be the nature of the process that converts the 7-line spectrum to a 4-line spectrum?
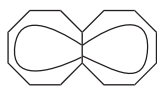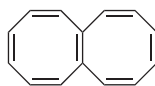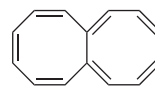
13-A   **13-B**   **13-C**

8.14. When alcohol **14-A** is dissolved in FSO$_3$H at $-136°$C and then brought to $-110°$C, it gives rise to a ^{13}C-NMR spectrum having five lines in the intensity ratio 2:1:2:2:2.

   a. Suggest several possible structures for this cation and discuss stabilizing features that might favor a particular structure.
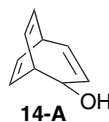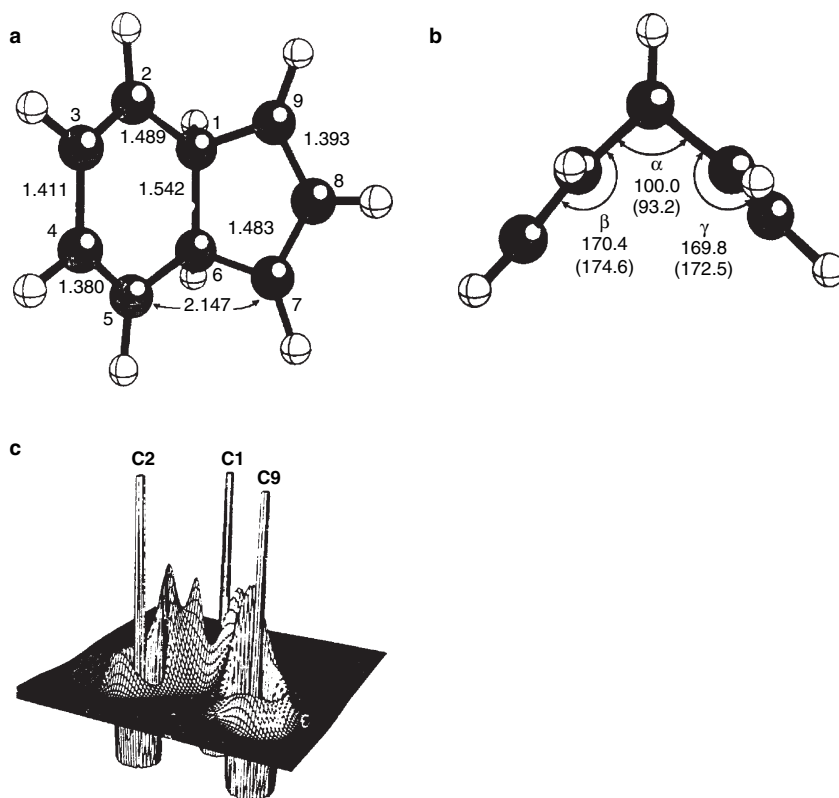

14-A OH

Fig. 8.P14. (a) Bond lengths and (b) inter-ring angles for minimum-energy cation; (c) $-\nabla^2\rho(\mathbf{r})$ in the C(1)−C(2)−C(9) plane. Reproduced by permission of the American Chemical Society Bond Orders: 1,2: 1.04; 2,3:1.59; 3,4: 1.57; 1,6:0.94; 1,9: 1.04; 8,9:1.56; 2,9:0.34.

b. Figure 8.P14(a, b) gives the computed minimum-energy structure at the MP4(SDQ)/6-31G(d) level. Diagram (c) is the $-\nabla^2\rho(\mathbf{r})$ in the C(1)−C(2)−C(9) plane. Does this structure correspond to any of those you have suggested in Part (a)? What structural representation would be most consistent with the calculated minimum-energy structure?

8.15. a. The heats of combustion (ΔH_c) and heats of hydrogenation (ΔH_{H_2}) for addition of 1 mol of H_2 and the estimated stabilization energy (SE) for benzene and cyclooctatetraene (in kcal/mol) are given below. The ΔH_c and ΔH_{H_2} are also given for [16]annulene. Compare the stabilization energy of [16]annulene with benzene and cyclooctatetraene on a per CH basis.

	Benzene	Cyclooctatetraene	[16]Annulene
ΔH_c	781	1086	2182
ΔH_{H_2}	−5.16	25.6	28.0
SE	36	4	?

b. The enthalpies of the reaction of the cyclooctatetraene and [16]annulene dianions with water have been measured.

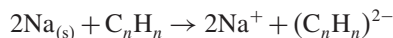$$2Na^+(C_nH_n)^{2-} + 2H_2O_{(l)} \rightarrow C_nH_{n+2} + 2NaOH$$
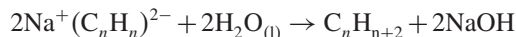
$$\Delta H = -33.33\,\text{kcal/mol for cyclooctatetraene}$$

$$\Delta H = -10.9\,\text{kcal/mol for [16]annulene.}$$

Using these data and the enthalpy of the reaction of sodium with water:
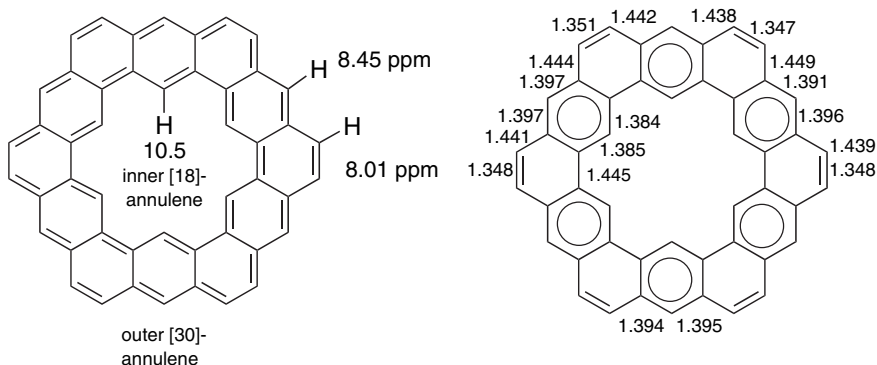
$$2Na_{(s)} + 2H_2O_{(l)} \rightarrow 2NaOH_{(aq)} + H_2 \quad \Delta H = -88.2\,\text{kcal/mol}$$

calculate ΔH for the reaction:
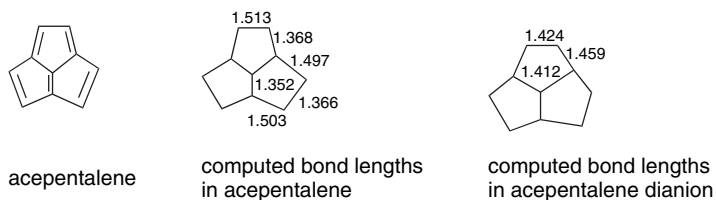
$$2Na_{(s)} + C_nH_n \rightarrow 2Na^+ + (C_nH_n)^{2-}$$

Why might the reaction of $[C_{16}H_{16}]^{2-}$ with water be less exothermic than for $[C_8H_8]^{2-}$? How do you interpret the difference in the heat of reaction of the two hydrocarbons to form the respective dianions?

8.16. Consider the two structures shown for kekulene, one suggesting inner and outer annulenes and the other a series of phenanthrene-like units. ^{1}H-NMR and bond length data are given. The NICS values are calculated as −4.3 for the angularly fused rings and −10.8 for the linearly fused rings. Indicate properties that you would expect to be associated with each structure. Do you consider the properties to be more consistent with the double-annulene or the phenanthrene-like structures?

H 8.45 ppm

H

H
10.5
inner [18]-
annulene

H

8.01 ppm

outer [30]-
annulene

1.351 1.442 1.438 1.347
1.444   1.449
1.397   1.391
1.397   1.384   1.396
1.441   1.385
1.348   1.445   1.439
             1.348
1.394 1.395

8.17. Acepentalene is a rather unstable molecule, but its dianion can be formed quite readily. The structure and properties of acepentalene and its dianion and dication have been calculated (B3LYP/6-31G*) and are given below. The computed lowest-energy structure is slightly pyramidal, with an inversion barrier of 7.1 kcal/mol. The structure of the lithium salt of the dianion is given in the Figure 8.P17. The calculated inversion barrier for the dianion is 5.4 kcal/mol. The chemical shift of the ^{1}H signal in the dianion is at -8.2.

1.513
1.368
1.497
1.352
1.366
1.503

1.424
1.459
1.412

acepentalene

computed bond lengths
in acepentalene

computed bond lengths
in acepentalene dianion

a. What evidence in terms of aromaticity/antiaromaticity can you offer for the apparently greater stability of the $12\,\pi$-electron dianion as compared with the $10\,\pi$-electron neutral? What accounts for the pyramidal as opposed to planar structures for the neutral and dianion?
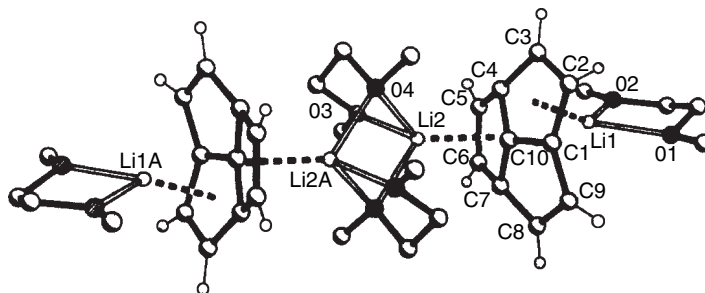

Fig. 8.P17. Crystal structure of Li$_2$(DME)$_2$acepentalenediide. Reproduced from *Angew. Chem. Int. Ed. Engl.*, **34**, 1492 (1995), by permission of Wiley-VCH.

|	NICS*	NICS$_{(in)}$ [a]	NICS$_{(out)}$ [a]	χ	Λ
Acepentalene	+42.3	50.0	31.0	−62.4	23.1
Dianion	−32.7	−42.3	−27.9	−141.0	−43.1
Dication	+10.2	−24.9	2.4	−72.9	−18.8

a. The NICS values are relative to positions 0.5 Å inside and outside the pyramidal structure. NICS* is the sum for all rings.

b. The HMO orbitals of acepentalene are given below. How do the predictions of HMO theory accord with the experimental and B3LYP results?

$$
\begin{array}{cc}
— & -2.086 \\
—\ \ — & -1.879 \\
— & -1.000 \\
—\ \ — & +0.347 \\
— & +0.572 \\
—\ \ — & +1.532 \\
— & +2.514
\end{array}
$$

8.18. Arene oxides are important intermediates in the metabolism of aromatic compounds. Although they are highly reactive, both valence tautomerism to oxepins and acid-catalyzed ring opening to phenols can be observed and studied.
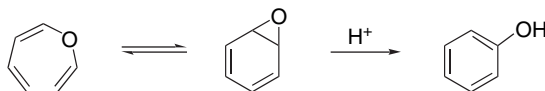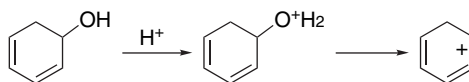

Surprisingly, the rate of acid-catalyzed ring opening is less than that for dehydration of "2,4-cyclohexadienol" even though they lead to similar cations. Normally, epoxide ring opening is much faster than alcohol dehydration. For example, the epoxide of cyclohexadiene is about 10^7 more reactive than cyclohexenol.
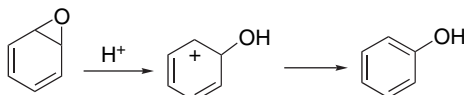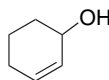

k [H$^+$][oxide] = 32 M^{-1}s^{-1}
$\Delta H_r = -57$ kcal/mol

k [H$^+$][dien-ol] = 190 M^{-1}s^{-1}
$\Delta H_r = -39$ kcal/mol

k [H$^+$][oxide] = 1.1 x 10^4 M^{-1}s^{-1} k [H$^+$][en-ol] = 10^{-3}M^{-1}s^{-1}

What might account for the apparent kinetic stability of the arene oxide toward acid-catalyzed ring opening?

8.19. Using isodesmic reactions and the G2(MP2) energies given below, determine if 1,2,3-trichlorocyclopropenium ion is more or less stable than the *tert*-butyl carbocation. Are the chlorine substituents stabilizing or destabilizing with respect to cyclopropenium ion?

Substance	G2(MP2) energy (hartrees)
Trichlorocyclopropenium	−1492.916633
Cyclopropenium ion	−115.492839
tert-Butyl carbocation	−157.169332
1,2,3,3-tetrachlorocyclopropene	−1952.950661
3-Chlorocyclopropene	−575.525577
tert-Butyl chloride	−617.226718

8.20. Triquinacene is a hydrocarbon that might be stabilized by homoaromaticity.
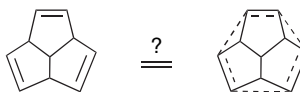
The calculated (B3LYP/6-3111+G*) ΔH_{H_2} for the successive double bond are −27.6, −27.3, and −26.8 kcal/mol. The ΔH_{H_2} for cyclopentene is −26.9 kcal/mol. The existence of homoaromatic stabilization of triquinacene might be assessed by the following homodesmotic reaction, where $\Delta E = -0.8$ kcal/mol:
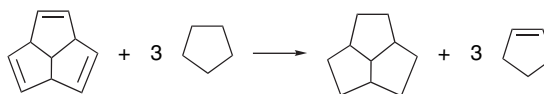
$\Delta E = -0.8$ kcal/mol

Do these data indicate homoaromatic stabilization of triquinacene? Why or why not?