Antiaromaticity in Monocyclic Conjugated Carbon Rings

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Contents

Kenneth Wiberg was born in Brooklyn, NY, in 1927. He studied chemistry at MIT and Columbia University and received his Ph.D. degree in 1950 working with William Doering. He was a faculty member at the University of Washington from 1950–1962, and then moved to Yale University where he was the Eugene Higgins Professor of Chemistry. His research interests include small ring chemistry, spectroscopy, physical organic chemistry, and computational chemistry.

1. Introduction

The development of wave mechanics by Schrödinger[1] in 1927 was quickly followed by molecular orbital theory.[2] The application of this method to conjugated unsaturated monocyclic hydrocarbons by E. Hückel in 1931,[3] making use of the π-electron approximation, led to the recognition that these compounds could be divided into two classes, those with $4n + 2$ π-electrons having bonding filled highest occupied MOs and those with $4n$ π-electrons where the corresponding MOs are nonbonding and half-filled. The latter leads to Jahn−Teller distortion,[4] giving a structure in which the degenerate orbitals are split in energy, with the π-electrons occupying the lower energy level. The net effect is to make the $4n + 2$ species relatively thermochemically stable, whereas the $4n$ species should be relatively unstable because the higher energy π-electrons are only weakly bound.

At the time of Hückel's work, benzene was the only known monocyclic $4n + 2$ molecule and it was recognized to be unusually stable. The MO picture was not familiar to organic chemists at that time, and Pauling's valence-bond approach[5] with its structural representations became the commonly used approach to "explain" the stability of benzene.[6] Although the $4n$ π-electron cyclooctatetraene was synthesized by Willstätter in 1911,[7] neither Hückel nor Pauling discussed it. It was found to be relatively reactive and to adopt a tub conformation in which the interactions between the double bond were minimized.[8] The difference between benzene and cyclooctatretraene cannot be explained by the simple valence-bond model.[9]

Further evidence for the $4n + 2$ rule was found in the observations that cyclopentadiene is unusually acidic[10] and that cycloheptatrienyl cation[11] and cyclopropenyl cation[12] are unusually stable in comparison to other carbocations. These observations led to the adoption of MO theory as the general approach to understanding the cyclic conjugated molecules.

The $4n$ π-electron molecule cyclobutadiene also was prepared[13] and found to be highly reactive and to adopt a rectangular D_{2h} geometry rather than the square D_{4h} geometry.[14] This is in accord with expectations based on the $4n + 2$ rule.

In 1967, Breslow, Brown, and Gajewski found that 1,2-diphenyl-3-benzoylcyclopropene underwent base-catalyzed H/D exchange at a slower rate than the corresponding cyclopropane by a factor of 6000.[15] Finding that the corresponding $4n$ anion was destabilized by a greater extent than might be expected, they proposed that it was "antiaromatic".[16]

As a result, there are now three classes of cyclic conjugated systems: those that are aromatic and have $4n + 2$ π-electrons, those that are nonaromatic and have $4n$ π-electrons, and those that are antiaromatic and have $4n$ π-electrons. Are the latter two distinct types of molecules, and is there a fundamental difference between them?

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Table 1. Calculated Energies, 6-311+G*[a]

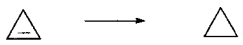
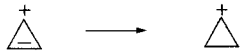
compound	ZPE	H_{corr}	B3LYP	MP2	CCSD(T)	G2
hydrogen	0.01001	0.01332	−1.17663	−1.14588	−1.15350	−1.16636
ethane (D_{3d})	0.07463	0.07906	−79.84841	−79.52651	−79.56862	−79.63090
ethene (C_{2v})	0.05083	0.05481	−78.60836	−78.31651	−78.35424	−78.41593
vinyl anion (C_s)	0.03544	0.03938	−77.94738	−77.65618	−77.69247	−77.76723
propane (C_{2v})	0.10331	0.10879	−119.17052	−118.70730	−118.76642	−118.85580
isopropyl radical (C_s)	0.08777	0.09402	−118.50556	−118.05394	−118.11076	−118.19887
isopropyl anion (C_s)	0.08563	0.09103	−118.49192	−118.02819	−118.08515	−118.19149
isopropyl cation (C_2)	0.08819	0.09407	−118.23376	−117.78742	−117.84558	−117.92706
allyl radical (C_{2v})	0.06590	0.07067	−117.28948	−116.86957	−116.91667	−117.00589
allyl anion (C_{2v})	0.06288	0.06823	−117.30326	−116.86722	−116.91515	−117.02516
allyl cation (C_{2v})	0.06834	0.07310	−116.99373	−116.58010	−116.63165	−116.70870
butane (C_{2h})	0.13181	0.13854	−158.49249	−157.88811	−157.96426	−158.08117
cis-2-butene (C_{2v})	0.10781	0.11432	−157.26086	−156.68414	−156.75478	−156.87190
cyclobutane (D_{2d})	0.11057	0.11561	−157.24612	−156.67736	−156.74555	−156.85860
cyclobutene (C_{2v})	0.08619	0.09096	−156.00764	−155.46763	−155.52975	−155.64388
cyclopropane (D_{3h})	0.08103	0.08534	−117.92100	−117.49302	−117.54317	−117.63121
cyclopropene (C_{2v})	0.05566	0.05989	−116.64605	−116.24734	−116.29164	−116.38129
cyclopropyl radical (C_s)	0.06651	0.07091	−117.23984	−116.82284	−116.87161	−116.95774
cyclopropyl anion (C_s)	0.06440	0.06875	−117.24903	−116.82285	−116.87058	−116.97480
cyclopropyl cation (C_{2v})	0.06402	0.06835	−116.93511	−116.52107	−116.57321	−116.65491
cyclopropenyl radical (C_s)	0.04214	0.04644	−115.97920	−115.59323	−115.63423	−115.72210
cyclopropenyl anion (C_s)	0.03867	0.04363	−115.96366	−115.56810	−115.61061	−115.71544
cyclopropenyl cation (D_{3h})	0.04497	0.04906	−115.75422	−115.38064	−115.42040	−115.49929
cyclobutadiene (D_{2h})	0.06077	0.06552	−154.71283	−154.20364	−154.26399	−154.37981
cyclopentadiene (C_{2v})	0.09221	0.09731	−194.14590	−193.49715	−193.56747	−193.70735
cyclopentadienyl radical (C_{2v})	0.07756	0.08334	−193.50640	−192.86759	−192.93362	−193.07381
cyclopentadienyl anion(D_{5h})	0.07785	0.08290	−193.56993	−192.93063	−192.98845	−193.14497
cyclopentadienyl cation (C_{2v})	0.07942	0.08487	−193.18885	−192.55576	−192.62891	−192.76009
dihydro radical (C_s)	0.10235	0.10802	−194.72956	−194.06145	−194.13466	−194.27107
dihydro anion (C_2)	0.09999	0.10548	−194.72928	−194.05555	−194.12664	−194.28218
dihydro cation (C_s)	0.10405	0.10949	−194.47849	−193.81479	−193.89242	−194.01967
pentadiene (C_2)	0.11306	0.12003	−195.34498	−194.65802	−194.74052	−194.88376
pentadienyl radical (C_{2v})	0.09977	0.10645	−194.72101	−194.04544	−194.11727	−194.26286
pentadienyl anion (C_{2v})	0.09709	0.10407	−194.75228	−194.05940	−194.13349	−194.29750
pentadienyl cation (C_{2v})	0.10276	0.10937	−194.45493	−193.78235	−193.86017	−193.99223
benzene (D_{6h})	0.10016	0.10555	−232.30070	−231.54045	−231.61414	−231.78053
1,3-cyclohexadiene (C_2)	0.12205	0.12817	−233.47174	−232.68076	−232.76943	−232.93515
cycloheptatriene (C_s)	0.12762	0.13432	−271.57164	−270.67228	−270.76671	
cycloheptatrienyl radical (C_{2v})	0.11233	0.11980	−270.94911	−270.03293		
cycloheptatrienyl anion (C_2)	0.11010	0.11741	−270.95602	−270.05492	−270.14618	
cycloheptatrienyl cation (C_{7h})	0.11885	0.12526	−270.72938	−269.84706	−269.93296	
dihydro radical (C_2)	0.13774	0.14495	−272.16133	−271.21392	−271.32959	
dihydro anion (C_2)	0.13476	0.14125	−272.18629	−271.25653	−271.35320	
dihydro cation (C_2)	0.13971	0.14700	−271.90793	−270.98916	−271.09166	
heptatriene (C_1)	0.14626	0.15543	−272.76564	−271.82357	−271.93350	
heptatrienyl radical (C_{2v})	0.13327	0.14204	−272.14962	−271.22025	−271.31354	
heptatrienyl anion (C_{2v})	0.13084	0.13982	−272.19344	−271.24383	−271.34383	
heptatrienyl cation (C_{2v})	0.13663	0.14529	−271.90150	−270.97123	−271.07498	
COT tub (D_{2d})	0.13212	0.13982	−309.65543	−308.64086		
COT planar[b] (D_{4h})	0.13317	0.14028	−309.63823	308.61455		
COT dianion (D_{8h})	0.12376	0.13212	−309.55420	−308.52346		
cyclooctatriene (C_1)	0.15653	0.16446	−310.88208	−309.83242		
cyclononatetraene (C_2)	0.16082	0.16984	−348.96275	−347.80845		
cyclononatetraenyl anion (D_{9h})	0.14838	0.15686	−348.41710	−347.26308		
cyclononatetraenyl radical (C_2)	0.14746	0.15668	−348.33627	−347.18350		
cyclononatetraenyl cation (C_2)	0.14955	0.15820	−348.08689	−346.96075		
cyclopentane (C_s)	0.14049	0.14573	−196.59880	−195.89114	−195.97555	−196.11425
cyclopentyl radical (C_2)	0.12565	0.13180	−195.93726	−195.24077	−195.32288	−195.46092
cyclopentyl anion (C_2)	0.12325	0.12928	−195.92668	−195.22111	−195.30266	−195.45772
cyclopentyl cation (C_2)	0.12548	0.13146	−195.67381	−194.98187	−195.06575	−195.19710

[a] Unless otherwise specified, the compounds have no imaginary frequencies. ZPE and ΔH_{corr} have been evaluated at the B3LYP/6-311+G* level, and CCSD(T) calculations used CCD/6-311+G* optimized geometries. [b] Planar cyclooctatetraene has an imaginary frequency.

2. "Aromaticity"

Before proceeding further, it should be made clear what is meant by aromaticity.[17] This is one of those concepts such as acidity for which most chemists have an intuitive understanding but which is difficult to define. Benzene is the prototype "aromatic" molecule, and based on it the following attributes of aromaticity have been proposed: (a) aromatic compounds have relatively low reactivity toward electrophiles, (b) aromatic compounds have relatively low energies, (c) aromatic compounds tend to have nearly

Table 2. Hydrogen Transfer Energies, 25 °C, kcal/mol

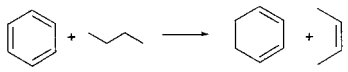
	B3LYP	MP2	CCSD(T)	G2	obs[32]
	-26	-25	-26	-26	-25.2±0.7
	29	37	32	34	
	-33	-31	-31	-32	
	-25	-17	-18	-27	
	-39	-37	-35	-35	-49±11
	-36	-34	-34	-32	~ -25
	44	49	44	45	
	6	7	6	7	
	37	39	33	35	34.0±0.4
	32	37	30		
	1	2	2		
	13	14			
	-8	-9			

equal C−C bond lengths, and (d) aromatic compounds have shielding nucleus-independent chemical shift (NICS) values at the center of their rings.

The reactivity criterion is less than satisfactory since many compounds that are generally recognized as aromatic are quite reactive. For example, both phenanthrene and anthracene will add bromine, and anthracene will undergo Diels−Alder additions. The bond length criterion is also not quite satisfactory since compounds such a naphthalene, anthracene, and phenanthrene have a range of bond lengths.[18]

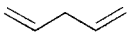
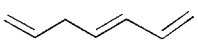
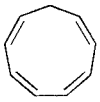
The thermochemical criterion has been generally applicable. There are two basic approaches. In the first, the heat of formation is compared with that of a nonconjugated model and the difference is taken as the "resonance energy".[19] The main problem is that of defining a suitable nonconjugated model. Depending on which model is chosen, the resonance energy of benzene ranges from 22 to 64 kcal/mol.[20] Fortunately, the relative resonance energies for a series of compounds are generally in the same order independent of the model chosen.

In many cases, the change in energy that results from adding hydrogen to one of the double bonds, thus breaking the cyclic conjugated system, may be used as a diagnostic tool. Using benzene as an example, the heat of reaction with butane to give 1,3-cyclohexadiene and *cis*-2-butene is[21] This reaction



was chosen rather than simple addition of hydrogen or hydrogen transfer from ethane since it leads to a "homisodesmic" reaction in which the bond types are retained on going from reactants to products.[22] This type of reaction will be useful in deriving such energies from the theoretical calculations since it tends to cancel deficiencies in the calculations. The highly endothermic reaction indicates the relative stability of benzene. A nonstabilized molecule should give a hydrogen transfer energy of about zero, whereas an antiaromatic compound should give an exothermic hydrogen transfer reaction. It should be

Table 3. Acidity Relative to Ethene, 25 °C, kcal/mol

Compound	B3LYP	MP2	CCSD(T)	G2	obs[32]
	13	11	12	11	
	6	5	6	5	3±2
	-53	-58	-51	-54	-55±3
	-43	-39	-35	-39	-40±4
	-30	-29	-27		-34±3
	-56	-51	-45		
	-71	-71			

remembered that the reduced product will often have some residual stabilization energy, and so the hydrogen transfer energies are minimum values for the stabilization of the compound in question.

Unfortunately experimental thermochemical data are available for only a few of the compounds of interest, and therefore, it is usually necessary to estimate reaction energies from theoretical calculations. There are many reports of theoretical calculations for the subjects of this review, but they make use of a variety of theoretical models and basis sets, and so it is often difficult to compare calculated reaction energies using a common model. The energies of the significant compounds have been recalculated via geometry optimizations at the B3LYP/6-311+G* and MP2/6-311+G* levels (Table 1).[23] In addition, geometry optimizations were carried out at the CCD/6-311+G* level followed by a CCSD(T)/6-311+G* calculations using these geometries. All of these calculations include correction for electron correlation, though by different methods. The CCSD(T) procedure is usually considered to be the more reliable method and was included because it has been found that B3LYP and MP2 gave inconsistent results for [10]annulene whereas CCSD(T) was satisfactory.[24] The results of these calculations will allow the methods to be compared. The basis set is reasonably flexible and includes diffuse functions that are needed to correctly describe anions.[25] The zero-point energies are derived from the B3LYP/6-311+G* calculations and are not scaled since this has been found to be unnecessary using this model. The H_{corr} values are the corrections to 25 °C and include the zero-point energy terms.

The G2 model chemistry of Pople, et al.[26] provides quite satisfactory energies for most organic molecules. When these energies are available,[27−30] they are included in the Table 1, and the energies for some of the charged species and radicals were calculated for this review. The G2 energies include the zero-point energies, and therefore, their correction to 25 °C makes use of the difference between H_{corr} and ZPE.

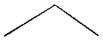
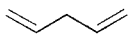
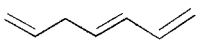
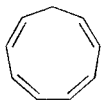
To make the calculated energies more useful, they have been converted into heats of reactions at 25 °C. Table 2 gives hydrogen transfer reaction energies using butane as the hydrogen transfer reagent. Table 3 gives acidities relative to ethene. The energies may be converted to ΔH_{acid} (25 °C) using the well determined ΔH_{acid} of ethylene, 409.4 ± 0.6 kcal/mol.[31] Table 4 gives the calculated C−H bond dissociation energies, and Table 5 gives the hydride transfer energies which are the enthalpies of reaction with isopropyl cation to give the product cation plus propane. Finally, Table 6 summarizes the energies of the electron transfer energies based on G2 energies when available and based on B3LYP/6-311+G* energies in the other cases. For the reactions where they can be compared, they give comparable energy changes (rms deviation = 2.5 kcal/mol). It can be seen that the reaction energies calculated at the different theoretical levels are generally in good agreement and are in agreement with the available experimental data.[32] The main deviations are found with the radicals (Table 5), where only G2 consistently gives C−H bond dissociation energies that are in good agreement with the observed values.[33] Among the other methods, B3LYP gives the more satisfactory dissociation energies.

In the case of the above hydrogen transfer to benzene, the calculated energy changes are given in Table 2. All of the values are in reasonable agreement with the experimental reaction enthalpy, and the G2 value is in very good agreement.

The NICS values developed by Schleyer et al.[34] represent some of the most interesting recent approaches to the study of aromaticity and antiaromaticity. They are the calculated shielding found at a point in the center of the ring in question; shielding is found for the $4n + 2$ systems, whereas deshielding is found for the $4n$ molecules. Although only the isotropic values have been reported, they have tensor components and it is interesting to examine them. The NICS values and their components for the compounds in this study are given in Table 7. In conformity with the work of Schleyer, they are given as the negative of the calculated shielding values.

The first entries are for the $4n + 2$ species. The conventional picture is that a current is induced in the π-system when the magnetic field is oriented perpendicular to the molecule. This leads to an induced magnetic field that is opposed to the applied field within the ring and is aligned with the field when it is outside the ring.[35] This has been proposed

Table 4. Secondary C−H Bond Dissociation Energies, kcal/mol[a]

Compound	B3LYP	MP2	CCSD(T)	G2	obs[33]
	94	87	88	99	98.6±0.4
	105	98	99	109	106.3±0.3
	96	88	90	100	91±4
	79	73	75	84	83±2
	69	62	69	76	
	68	79			77±3
	64	56	67		
	71	70			

[a] The PMP2 radical energies were used, and the energy of a hydrogen atom was taken as −0.5 H in each case.

to account for the downfield shift of the benzene protons[36] and for the observation that protons lying above a benzene ring experience an upfield shift.[37]

However, the results for $C_3H_3^+$ and $C_5H_5^-$ are not in accord with this simple picture since the terms about the in-plane axes and the value about the out-of-plane axis are quite similar. The problems with the simple ring current approach has been reviewed by Fleischer et al.[38] A further indication of problems with this simple approach is found with cyclopropane, where the NICS shielding is greater than for any of the $4n + 2$ systems. This might be related to the proposed "σ-aromaticity" of the cyclopropane ring,[39] although it remains a subject of considerable controversy.[40] Here, it might be noted that much of the stability of the cyclopropane ring is associated with the large C−H bond energies.[41]

On the other hand, most of the $4n$ systems give large NICS deshielding values and the major component does lie along the axis perpendicular to the ring. However, even here there are some problems. Planar cyclobutane has a positive NICS value, and the largest deshielding term corresponds to the out-of-plane axis. Further, the NICS value for cyclopropenyl anion is negative, whereas it would be expected to be positive. However, if the ring is forced to be planar, the NICS value becomes positive.

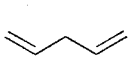
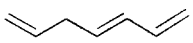
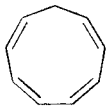
It is clear that the NICS approach requires further study. It will be important to identify which occupied-virtual MO pairs lead to the large deshielding terms for the $4n$ systems. In the case of the $4n + 2$ systems, the NICS values are the sum of both diamagnetic and paramagnetic terms and it will be necessary to examine their origins.[42]

The conclusion is that the thermochemical approach is the only one that is, at present, able to give detailed information about the cyclic conjugated molecules. Thus, this will be the major emphasis in the following sections.

3. Cyclopropenyl Anion

The synthesis of triphenylcyclopropenium ion and related cyclopropenium ions by Breslow,[12] coupled with its low reactivity toward nucleophiles, in contrast to other carbocations, demonstrates that the $4n + 2$ rule applies even when $n = 0$. The heat of formation of cyclopropenium ion has been determined from the heat of combustion of cyclopropene and the mass spectrometric appearance potential of the $C_3H_3^+$ ion[43] and indicates considerable stability. This led to an interest in the cyclopropenyl anion, which should not have any significant π-stabilization. As noted

Table 5. Hydride Transfer Energies, 25 °C, kcal/mol[a]

Compound	B3LYP	MP2	CCSD(T)	G2	obs
	29	31	29	30	+26±5
	-26	-31	-29	-30	-25±5
	14	15	13	12	~ +4±10
	-27	-25	-23	-24	~ -14±10
	-56	-56	-51		-55±5
	-43	-40	-36		
	-36	-43			

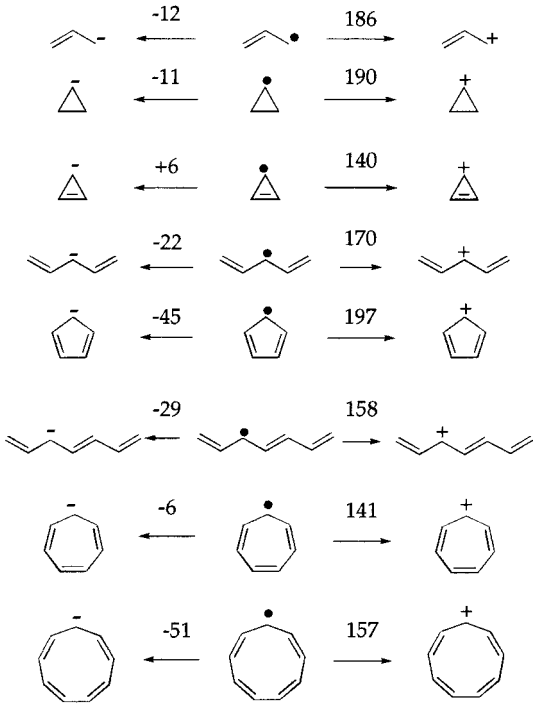
[a] Calculated enthalpies of reaction with isopropyl cation at 25 °C.

above, Breslow showed that proton abstraction from the methylene group of 1,2-diphenyl-3-benzoylcyclopropene is exceptionally difficult,[15] and other possible precursors such as tri-*p*-nitrophenylcyclopropene have been examined with similar results.[44] It is clear that these compounds are much less acidic than the corresponding cyclopropanes, and one might estimate the difference as ~5 kcal/mol. This led to the proposal that this ion is "antiaromatic", being less stable than expected for an anion that just lacked π-stabilization.

Subsequently, the electrochemical reduction of a cyclopropenium ion using second harmonic AC voltammetry was studied.[45] This led to an estimated pK_a of 61.3 ± 0.5 for cyclopropene as compared to 38.8 ± 0.4 for cycloheptatriene, which corresponds to a difference in acidity of 31 kcal/mol. The calculated gas-phase value (Table 3) is somewhat higher (43 kcal/mol), but the difference will probably be smaller in solution because the small cyclopropenyl anion should be better stabilized by a solvent than is the larger cycloheptatrienyl anion.

Theoretical calculations (see below) lead to a nonplanar geometry for the ion, and this raises the question of whether the geometry is fixed or if the ring can undergo pseudorotation which would make the carbons equivalent on any reasonable time scale. This question was examined by Borden et al., who showed that ^{13}C-labeled triphenylcyclopropenyl anion, formed via the fluorodesilylation of **1**, underwent

Table 6. G2 Energies of Electron Transfer Reactions, kcal/mol[a]

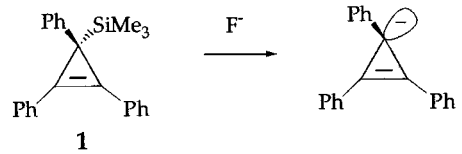


[a] The energies for the C7 and C9 compounds are based on B3LYP/6-311+G* energies.

Table 7. Calculated NICS Components, GIAO/B3LYP/6-311+G*

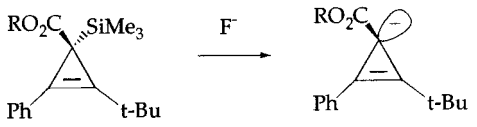
compound	$\sigma_{x,z}$	σ_y	σ_{iso}
$C_3H_3^+$	−18.6	−29.9	−22.4
$C_5H_5^-$	−10.9	−15.9	−12.5
benzene	−4.8	−14.0	−7.9
$C_7H_7^+$	−1.1	−15.7	−6.0
$C_8H_8^{-2}$	0.7	−39.3	−12.7
$C_9H_9^-$	−1.0	−38.6	−13.6
C_3H_6	−48.6	−29.5	−42.4
C_4H_8, planar	−26.0	61.2	3.1
$C_3H_3^-$	−20.5	12.2	−9.6
C_4H_4	−15.0	115.9	28.7
$C_5H_5^+$	−0.5	261.4	86.8
$C_7H_7^-$	−2.5	485.9	160.3
C_8H_8, planar	−2.4	127.9	41.0

carbon scrambling before it abstracted a proton from the medium to form triphenylcyclopropene.[46]



1

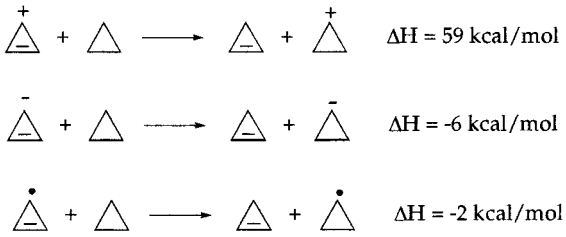
Kass and Sachs reported the first direct evidence for the formation of a cyclopropenyl anion via the fluoride ion desilylation of **2** in the gas phase.[47] Subsequently, it was possible to demonstrate the existence in solution of 1-phenyl-2-*tert*-butylcyclopropenyl-1-carboxylate via UV spectroscopy.[48] When the reactant was optically active, the product of trapping with benzaldehyde was racemic. Thus, a substituted ion may be observed experimentally and its reactions may be studied.



2

The ΔH_{acid} of methyl cyclopropene-3-carboxylate has been measured, and it is 391 ± 4 kcal/mol,[49] which may be compared with that of methyl cyclopropanecarboxylate (377 ± 4 kcal/mol). Thus, it is 14 kcal/mol less acidic than the saturated ester.

The cyclopropenyl anion has been the subject of many theoretical studies,[50,51] and the main conclusion is that it adopts a nonplanar configuration which minimizes the interaction of the anionic lone-pair electrons with the C−C π-bond. Glukhovtsev, Laiter, and Pross[28] carried out a careful study of the cyclopropenyl system at the G2 theoretical level. They showed that these calculations reproduced the available experimental data, such as the enthalpy of formation of the cyclopropenium ion, and then made use of a series of isodesmic reactions to explore the stability of the species:



These energies may also be obtained from the data in Table 2, but here one must correct for the very large enthalpy of hydrogenation of cyclopropene, as compared to *cis*-2-butene.

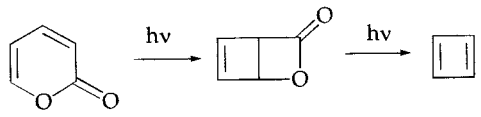
The data show that cyclopropenyl cation is remarkably well stabilized, that the anion is somewhat destabilized, and that the radical is essentially unstabilized. This may also be seen in comparing the ionization energies and electron affinities of allyl radical and cyclopropenyl radical in Table 6. Here, the cyclopropenyl cation is 46 kcal/mol more easily formed than allyl cation, but the cyclopropenyl anion is 18 kcal/mol less easily formed than allyl anion. The two allyl ion have, of course, some stabilization energies, and correction for this would increase the stabilization for the cation and decrease the destabilization for the anion. Thus, all of the data are in good accord.

It might be noted that the calculated destabilization of the anion based on the acidity (Table 3, 6 kcal/mol) is in very good agreement with the estimate derived from the base-catalyzed H/D exchange reactions. The fully antiaromatic ion would be planar, and a calculation for this anion found three imaginary frequencies (two associated with hydrogen out-of-plane bends and one in-plane mode). Its G2 energy is 34 kcal/mol higher than that of the nonplanar ion.

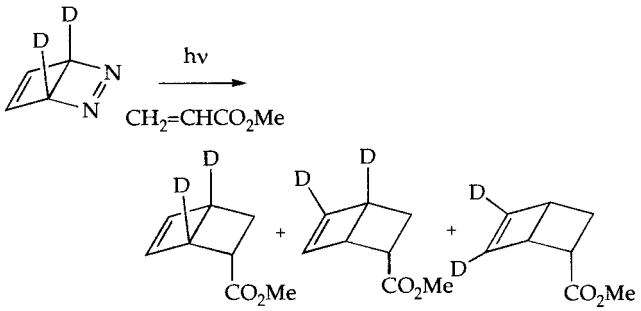
Merrill and Kass presented a detailed theoretical study of substituent effects on the cyclopropenyl anion.[52] Cyano substituents were found to be particularly effective in stabilizing the anion, and the tricyano compound was calculated to be stabilized by 74 kcal/mol! Breslow [43] tried to prepare tricyanocyclopropenyl anion, but other products were formed.

4. Cyclobutadiene

Cyclobutadiene is a key compound in the study of antiaromaticity since it is the smallest neutral example and it is planar. Its chemistry has been the subject of several reviews.[53] It was first observed in an argon matrix, being formed by the photolysis of α-pyrone.[54] Subsequently, it was prepared from a variety of other precursors.[53] It is highly reactive, and it readily dimerizes when the matrix softens and molecular diffusion becomes important. The dimerization process has been studied theoretically.[55] Although cyclobutadiene cannot be isolated in the pure form, it can be stabilized by the formation of metal complexes.[56]



Since the square D_{4h} structure has a half-filled degenerate pair of π-MOs, one might expect it to be subject to Jahn−Teller distortion,[4] which would lift the degeneracy. The first chemical evidence that it has a rectangular D_{2h} structure rather than the square D_{4h} geometry was obtained by the formation of a 1,2-dideuterium-substituted derivative and trapping it with methyl acrylate and with methyl-(*Z*)-3-cyanoacrylate.[57] With methyl acrylate, four products were formed corresponding to addition to both cyclobutadiene-1,2-d_2 and -1,4-d_2, but with the cyanoacrylate, a single product derived from cyclobutadiene-1,2-d_2 was found. This showed that the rate of interconversion of the cyclobutadienes was comparable to the rate of trapping.

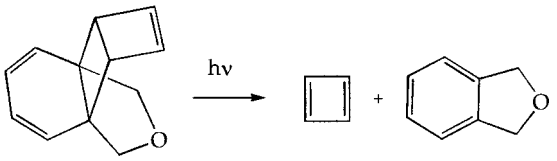


In contrast to cyclobutadiene, tri-*tert*-butylcyclobutadiene is a stable compound.[58] The equilibrium between the two double-bond isomers cannot be frozen out in a ^{13}C NMR experiment at 88 K. This suggests the activation energy for the process is less than 2.5 kcal/mol. A similar conclusion was derived using the isotopic perturbation method of Saunders[59] and examining the ^{13}C NMR spectrum of vicinally ^{13}C-dilabeled cyclobutadiene.[60] Here, the rate of interconversion exceeds 10^3 s^{-1} at 25 K.

The X-ray structure of tetra-*tert*-butylcyclobutadiene at room temperature shows relatively little difference between the C−C bond lengths. However, at −150 °C, it has significantly different observed

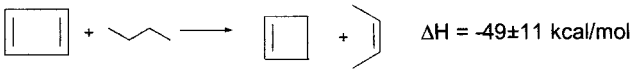
bond lengths of 1.441 and 1.526 Å, clearly showing its rectangular structure.[61] The similarity of bond lengths at room temperature is presumably caused by interconversion through the square structure, a process that is believed to occur via heavy atom tunneling.[62]

The heat of formation of cyclobutadiene is an especially important quantity with regard to the question of whether of not it is antiaromatic. A number of experimental approaches were examined, but they were only able to give an approximate value.[63] Recently, its heat of formation was estimated by photoacoustic calorimetry.[64] Here, **3** was photolyzed in solution via a laser pulse and the energy released in the reaction is converted to heat, which leads to an expansion of the irradiated region of the solution. The resulting pressure pulse can be observed by an acoustic transducer (microphone). By the use of suitable calibration, the heat of the reaction was determined to be 25 ± 10 kcal/mol. The heats of formation of the reactant and product were estimated, and a heat of formation of cyclobutadiene was calculated to be 114 ± 11 kcal/mol.



3

The enthalpy change for the transfer of two hydrogens is then available: The enthalpy change is



large and exothermic, in marked contrast to the endothermic reaction of benzene noted above. It is not likely that the energy change has a large component of strain release since the corresponding reaction of cyclobutene is close to thermoneutral (calcd, −3.4 kcal/mol (G2); obsd, −2.5 ± 0.4 kcal/mol).

Cyclobutadiene has been the subject of a large number of theoretical calculations including semiempirical,[65] ab initio,[66] and G2.[67] The calculated enthalpy changes for the above reaction are given in Table 2. They are uniformly less exothermic than the experimental value. It seems unlikely that there is such a large error in all of the calculated values. Perhaps the estimates of the energies of the reactant and product in the experimental study are in error. Thus, it is concluded that cyclobutadiene is destabilized by 35 kcal/mol.

It is interesting to note that calculations by Borden found that singlet cyclobutadiene has a lower energy than the triplet at all geometries, suggesting that Jahn−Teller distortion is not important in this case.[68] Rather, the stability of the singlet is a result of configuration interaction among singlet configurations which is especially effective with molecules having this symmetry.

5. Cyclopentadienyl Cation

The acidity of cyclopentadiene was recognized as early as 1900,[10] and its anion is a common chemical reagent. The acidity relative to ethylene has been determined experimentally and is −55 ± 3 kcal/mol.[30] The calculations in Table 3 are in very good agreement with the experimental value and show that it is stabilized by about 55 kcal/mol. The stabilization has two components: the π-electron stabilization and the stabilization in the gas phase of a larger anion as compared to a vinyl anion. The stabilization may also be seen in the data in Table 2. The hydrogen transfer energy is somewhat smaller, but it should be remembered that the cyclopentenyl anion will be stabilized as are all allyl anions.

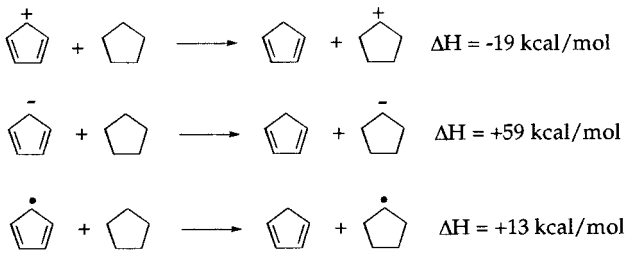
The general recognition of the difference between the $4n + 2$ and $4n$ π-systems led to many studies of the cyclopentadienyl cation. In an early observation, Breslow et al. reported that cyclopentadienyl halides are remarkably resistant to solvolysis.[69] Thus, cyclopentadienyl iodide does not react with silver perchlorate in propionic acid solution. Subsequently, it has been possible to prepare substituted cyclopentadienyl derivatives which undergo solvolysis, but the rates of reaction are very low.[70] Cyclopropyl substituents appear to be particularly effective in stabilizing the cation.[71]

The ESR spectrum of the unsubstituted ion has been observed in di-*n*-butyl phthalate by the reaction of 5-bromocyclopentadiene with SbF_5 at 78 K, and it was shown to be a triplet.[72] The enthalpy of formation is ∼252 ± 10 kcal/mol was estimated from mass spectrometric studies.[32] It has been possible to observe the IR spectrum of matrix-isolated pentachlorocyclopentadienyl cation.[73]

The cation has received extensive theoretical treatment,[34,74−76] and the triplet was found to have the lower energy, although with a small singlet−triplet gap. Many structures have been suggested for the singlet ion,[77] but there is now agreement that a planar ion with C_{2v} symmetry has the lower energy. Jahn−Teller distortion of the symmetrical cation will lead to two modes of distortion and two lower symmetry structures for the ion. However, the energy difference between them is very small. Using several different approaches, the destabilization of the cation has been estimated to be 31 kcal/mol. The hydrogen transfer energy in Table 2 agrees with this estimate. However, the latter also includes the stabilization of cyclopentenyl cation, and thus, the stabilization should be somewhat smaller.

One way to eliminate the effect of stabilization of the cyclopentenyl products is to make use of reactions such as those noted above for the cyclopropenyl series. The G2 energy changes are[78] Not surprisingly, the radical is somewhat stabilized. The anion is greatly stabilized, and the cation is more destabilized than the cyclopropenyl anion. This should be expected since the cation is planar, forcing the π-orbitals to interact with each other, whereas cyclopropenyl anion is nonplanar, thus minimizing π-electron interactions.

Substituent effects for the cation have been calculated using MP2 and MM2,[79] and it was found that



alkylated cyclopentadienyl cations prefer one of the two possible isomeric forms of the cation.

6. Cycloheptatrienyl Anion

Cycoheptatrienylium bromide was first prepared by Merling,[80] but it was not recognized as such until the work of Doering and Knox.[81] Experimental data including IR, Raman, and ^{1}H NMR spectroscopies and X-ray crystallography[82] showed that it has a planar D_{7h} structure. The enthalpy of formation has been determined by mass spectroscopy and is 208 ± 5 kcal/mol at 25 °C.[31] Theoretical calculations are in agreement with these data (cf. Table 5) and suggest that it is stabilized by about 55 kcal/mol. A part of this stabilization may be attributed to its larger size than the isopropyl cation. The hydrogen transfer energy is 30 kcal/mol, which is a minimum stabilization energy since the product cycloheptadienyl cation will have significant stabilization. A reasonable estimate of the stabilization is about 50 kcal/mol.

The 4*n* cycloheptatrienide anion was obtained by the treatment of 7-methoxycycloheptatriene with K−Na alloy in THF at −20 °C and has high reactivity.[83] NMR spectroscopy of some monosubstituted derivatives showed that they have nonplanar structures, in contrast to the cation.[84] The ΔH_{acid} of cycloheptatriene is 375 ± 3 kcal/mol,[31] making it 34 ± 3 kcal/mol more acidic than ethylene. The calculated values in Table 3 are in good agreement with this difference. This is in sharp contrast with cyclopropene, which is 11 kcal/mol less acidic than ethylene. A number of calculations have been reported for cycloheptatrienyl anion,[85] as well as studies of its formation and reactions in the gas phase.[86]

The hydrogen transfer energy (Table 2) for cycloheptatrienyl anion is very small, suggesting that it is essentially unstabilized. The same conclusion may be reached using the data in Table 6. Here, the formation of the anion is 23 kcal/mol less exothermic than for the heptatrienyl anion. The formation of the latter anion is 17 kcal/mol more exothermic than for the allyl anion, and if this ion has ∼10 kcal/mol stabilization, the heptatrienyl anion will be stabilized by about 25 kcal/mol and leads to the conclusion that there is no significant stabilization or destabilization for the cycloheptatrienyl anion. This presumably is at least in part a result of the puckered geometry of the anion. The cycloheptatrienyl radical has some stabilization.

7. Cyclooctatetraene

Cyclooctatetraene is the first 4*n* π-electron hydrocarbon to be studied.[7] Unlike benzene, it is highly reactive toward bromine and other electrophiles, and when the structure was determined by electron diffraction, it was found to adopt a "tub" conformation that will minimize the interaction between the double bonds.[8] Here, the torsional angle between the double bonds is 54°. An important observation is that it undergoes thermal bond shift and ring inversion processes.[87] Substituent effects on the bond shift has been studied.[88]

The ring inversion presumably involves a planar D_{4h} transition state having alternate single and double bonds, and the bond shift is believed to proceed via a planar D_{8h} transition state in which all of the C−C bonds become equal in length.[89] The inversion barrier has been measured in the gas phase for cyclooctatetraene via a measurement of the electron affinity of COT and was found to be 12.7 ± 0.5 kcal/mol.[90] The bond shift process has a somewhat higher barrier, 14 kcal/mol.[68] The antiaromatic destabilization of the D_{8h} form is then about 2 kcal/mol Theoretical calculations[91] are in good accord with the experimental results.

The data in Table 1 leads to an energy difference between the tub and D_{4h} planar structure of 11 kcal/mol (B3LYP) or 17 kcal/mol (MP2), much of which can be accounted for by the increased strain in the planar structure. The hydrogen transfer energy for the planar structure going to cyclooctatriene is calculated to be −8 kcal/mol (B3LYP) and −9 kcal/mol (MP2). All of the data indicate a relatively small antiaromatic destabilization for the puckered form of this tetraene.

It is interesting to note that the planar D_{4h} structure can be stabilized by perfluorocyclobutano annelation,[92] whereas the perfluorocyclopentano compound adopts the tub conformation. Apparently, the large external bond angles at a cyclobutene double bond are able to accommodate the large C−C−C bond angles of planar cyclooctatetraene, whereas the smaller angles for a cyclopentene are not able to do so.

Cyclooctatetraene readily adds two electrons in solution to form the 4*n* + 2 π-electron dianion. Despite the large C−C−C bond angles (144°), it adopts a planar D_{8h} structure according to the NMR spectrum. Ab initio calculations for this ion give a planar D_{8h} structure using B3LYP/6-311+G**,[93] but at the B3LYP/6-311+G* level, the D_{8h} structure is found to be a transition state. Here, the ion is calculated to be slightly puckered with C−C−C−C torsional angles of 1.8°. MP2 calculations give a puckered structure using both basis sets (8.7° with 6-311+G** and 9.6° with 6-311+G*). The difference in energy between the puckered and planar forms is very small, and it will appear planar in most experiments.

8. Cyclononatetraenyl Cation

The 4*n* + 2 cyclononatetraenyl system is the anion which is prepared by the reaction of chlorobicyclo-[6.1.0]nonatetraene with potassium.[94] The planar D_{9h} structure has been confirmed by low-temperature ^{1}H NMR spectroscopy.[95] This is remarkable in view of the 140 °C−C−C bond angles, which lead to consid-

erable strain and indicate the strong conjugation energy in the anion. The gas-phase energy of the ion does not appear to have been determined. Theoretical calculations at a relatively low level have been reported[96] and agree with the experimental observations. Cyclononatetraene is calculated to be 71 kcal/mol more acidic than ethylene (Table 3). Thus, it is significantly more acidic in the gas phase than cyclopentadiene, and at least a part of the difference must result from its larger size. Further, in Table 6, the conversion of the radical to an anion is equally exothermic for the C5 and C9 cases. It appears that the C5, C7, and C9 $4n + 2$ species have similar stabilization.

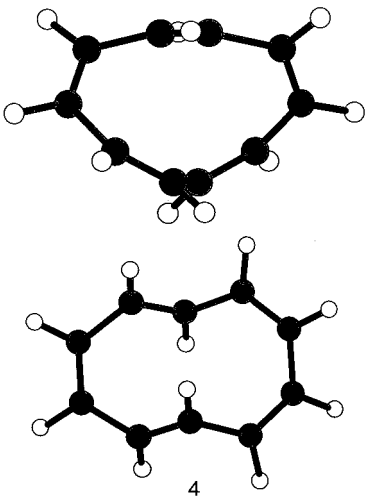
The $4n$ cyclononatetraenyl cation was studied by Anastassiou and Yakali via the treatment of deuterium-labeled 9-chlorocyclononatetraene with liquid SO_2 (an ionizing solvent), and they found that the deuterium became statistically distributed, presumably via the cation.[97] They wondered why this $4n$ system could be so easily formed and proposed a helical geometry. Subsequent calculations by Schleyer et al.[98] found that the lowest energy conformation of the ion did have a structure of this type, which leads to a Möbius π-electron system in which there is one inversion of phase. Compounds of this type were predicted by Heilbronner to have aromatic character,[99] and the NICS value for this ion is in accord with this expectation. Calculations for other conformations of this ion have been reported.[98]

The data in Tables 5 and 6 provide information on the stability of the cation. The reaction of cyclononatetraene with isopropyl cation is calculated to be exothermic by −36 kcal/mol, which may be compared with the reaction of cyclopentadiene which is endothermic by 14 kcal/mol. In fact, the reaction of cyclononatetraene is only 20 kcal/mol less exothermic than that of cycloheptratriene despite the latter being a $4n + 2$ system. It appears that the cyclononatetraenyl cation should be considered to be a strained aromatic system.

9. The Higher Annulenes

[10]Annulene, a $4n + 2$ π-system, was first prepared by Masamune and Burkoth in 1971, and two isomers were isolated.[100] A total of six structures have been suggested,[101] and it is generally agreed that the all-cis planar structures (D_{10h} and D_{5h}) have relatively high energies because of their 144 °C−C−C bond angles. Thus, [10]annulene and the higher annulenes have some trans-double bonds and as a result have some hydrogens that are inside the carbon skeleton. The NMR spectrum of one of the isomers had a single peak for both the ^{1}H and ^{13}C spectra down to −160 °C, indicating a rapid process that makes all of the CH groups equivalent. The ^{13}C spectrum of the other isomer separated into five distinct peaks at −100 °C.

Many computational attempts to resolve the conformational problem have been reported.[102] A recent study by King, Crawford, Stanton, and Schaefer[24] found that the relative energies calculated at the B3LYP and MP2 levels were inconsistent and concluded that CCSD(T) was required in order to obtain correct relative energies. The structures of the minimum energy C_2 twist form and the next higher energy C_2 naphthalene-like form (with an energy 1.3−2.0 kcal/mol higher) are shown in Figure 1.



4

Figure 1. Structures of the low-energy conformers of [10]-annulene.

These structures reveal that [10]annulene has markedly reduced π-conjugation, along with considerable strain energy. For example, the torsional angles of structure **4** are 0.4°, 124.7°, −151.1°, 40.9°, −7.5°, 40.9°, −151.1°, 124.7°, 0.4°, and −37.3° and the bond lengths alternate between 1.36 and 1.37 and 1.48−1.49 Å.

However, Schleyer et al.[103] predicted that the planar D_{5h} structure could be stabilized by fusing cyclopropane or cyclobutane rings to the C−C bonds. These small rings have large external bond angles that could accommodate the large C−C−C bond angles in the annulene. The resulting structures were calculated to have a NICS chemical shift corresponding to that for a stabilized $4n + 2$ species, and they were calculated to have significant π-electron stabilization.

The $4n$ π-electron [12]annulene has received little study and does not appear to have been prepared. It might be expected to have the same difficulty as the [10]propellane in achieving a conformation in which the double bonds could interact, and it would be expected to be further destabilized since it is a $4n$ system.

The [14], [16], and [18]annulenes have been prepared and extensively studied. In [14]annulene, the four inner hydrogens repel each other, therefore forcing the carbon ring to become nonplanar. This has been found both in an X-ray study[104] and via semiempirical calculations.[105] The larger [18]annulene has six inner hydrogens that interact weakly, leading to an essentially planar structure.[106]

Some calculations for these $4n + 2$ π-electron systems are shown in Table 8. It is possible to make a direct comparison of benzene and [18]annulene since if they were equally stabilized the energy of the latter would be three times that of the former. However, [18]annulene is calculated to be 71 kcal/mol less stable than three benzenes. Thus, its stabilization is on the order of 30 kcal/mol or about one-third that of benzene on a per π-electron basis. The

Table 8. B3LYP/6-311+G* Calculated Energies of Annulenes

compound	ZPE	H_{corr}[a]	B3LYP/6-311+G* calcd	B3LYP/6-311+G* with H_{corr}	ΔH (kcal/mol) H trans.
[14]annulene	0.23558	0.24883	−541.92625	−541.67742	17
dihydro[14}annulene	0.25804	0.27225	−543.13461	−542.85739	
[16]annulene	0.26907	0.28467	−619.34702	−619.06235	9
dihydro-[16]annulene	0.29203	0.30822	−620.56369	−620.25537	
[18]annulene	0.30170	0.32013	−696.79226	−696.47213	24
dihydro[18]annulene	0.32522	0.34399	−697.98547	−697.64148	
butane		0.13854	−158.49248	−158.35395	
cis-2-butene		0.11432	−157.26086	−157.14654	

[a] Sum of the zero-point energy and the enthalpy correction to 25 °C.

stabilization may also be estimated by examining the hydrogen transfer energy leading to the reduction one of the external cis-double bonds, and it is found to be 24 kcal/mol (Table 8).

[18]Annulene possesses conformational mobility associated with the interchange of positions of the inner and outer hydrogens. If it is assumed that aromatic stabilization will be lost in this process, the stabilization of the annulene would be about 16 kcal/mol.[107]

[14]Annulene has significant strain associated with the repulsion of the inner hydrogens. Again, using a comparison with benzene, if both molecules were equally stabilized, the energy of the annulene would be 2.33 times that of benzene. However, this comparison indicates that it is about 70 kcal/mol less stable than predicted, and thus, it has less net stabilization than [18]annulene. The smaller hydrogen transfer energy (17 kcal/mol, Table 8) is in accord with this estimate.

The $4n$ π-electron [16]annulene may be compared with benzene in the same fashion, and it is found to be 78 kcal/mol less stable than predicted, a larger value than for the other two annulenes. The hydrogen transfer energy (Table 8) also is much smaller than that of the other annulenes.

It seems clear that [14] and [18]annulenes have significantly less aromatic character than the smaller ring $4n + 2$ π-electron systems and that [16]annulene has little if any antiaromatic character.

10. Summary

The stabilization energies of the $4n + 2$ species and the destabilization energies of the $4n$ species are given in Table 9.

The $4n + 2$ ions appear to have essentially the same stabilization, on the order of 50 kcal/mol, which represents a decreasing stabilization per π-electron with increasing ring size. Benzene is somewhat less stabilized, and [18]annulene is still less stabilized but with three times as many π-electrons as benzene.

The smaller $4n$ species are markedly destabilized if they are planar. However, they prefer nonplanar geometries, and then the antiaromatic destabilization is greatly reduced. When the ring size becomes larger, the antiaromatic character is decreased and is small even with cyclooctatetraene.

11. Triplet States

Baird noted that the Hückel rules should be reversed in the triplet states, so that the $4n$ π-electron systems become "aromatic" whereas the $4n + 2$ systems either have reduced stability or become "antiaromatic".[108] A simple consideration of the ground state of cyclobutadiene is that the square D_{4h} structure has a half-filled degenerate π-level, which may leads to Jahn−Teller distortion to the rectangular D_{2h} structure (however, see below). In the triplet state, the two highest energy π-electrons are required to occupy different orbitals since they have the same spin. As a result, the square geometry with its degenerate π-orbitals can accept these electrons, and it is calculated to be the minimum energy structure for the triplet.[109]

Table 9. Calculated Stabilization Energies for $4n + 2$ Species and Destabilization Energies for $4n$ Species

ring size	$4n + 2$	$4n$
3	−59	+6 (+40, planar)
4		+35
5	−48	+29
6	−34	
7	−50	∼0
8		+4
9	−50	*a*
14	∼−10 (*b*)	
16		∼0
18	∼−25	

[a] The cyclononatetraenyl cation adopts a Möbius geometry, see text. [b] The π-stabilization is reduced by a significant strain energy.

If one of the double bonds of the cyclobutadiene triplet state were reduced, the product would be the triplet state of cyclobutene, having a high energy. NICS calculations by Schleyer et al. found shielding values characteristic of aromatic species.[110] Thus, by any criterion, the triplet state of cyclobutadiene has "aromatic" character.

The singlet and triplet states of cyclobutadiene lie close in energy. Here, one might expect the triplet to have the lower energy, but configuration interaction among the singlet configurations drops the singlet below the triplet in energy for all geometries.[68,109] The calculated singlet−triplet gap is 10 kcal/mol at the G2 level (Table 10), which compares favorably with the experimental value (12 kcal/mol) for a peralkylated cyclobutadiene.[111]

The case of benzene is quite different. Here, the degenerate π-level is filled in the singlet. As a result, in the triplet, one of the electrons must be promoted into one of the virtual π-orbitals. This leads to Jahn−Teller distortion in the triplet, and the lowest energy triplet is calculated to have an elongated D_{2h} geom-

Table 10. Energies of Triplet States

compound	symmetry[a]		ZPE[b]	B3LYP[b]	G2[b]	T−S (kcal/mol)[c] B3LYP	T−S (kcal/mol)[c] G2
cyclopropenyl anion	C_s	C_{3v}	0.03945	−115.95768	−115.69870	14.6	13.0
cyclobutadiene	D_{2h}	D_{4h}	0.05937	−154.70362	−154.35945	10.8	10.0
cyclopentadienyl cation	C_{2v}	D_{5h}	0.08054	−193.20574	−192.76478	−9.2	−2.9
cyclopentadienyl anion	D_{5h}	C_s	0.07627	−193.45968		68.2	
benzene	D_{6h}	D_{2h}	0.09180	−232.16992		76.8	
cycloheptatrienyl cation	D_{7h}	C_2	0.11181	−270.60666		72.6	
cycloheptatrientyl anion	C_2	D_{7h}	0.11077	−270.95993		−1.9	
cyclooctatetraene	D_{2d}	D_{8h}	0.13329	−309.63825		15.6	24[d]
cyclononatetraenyl cation	C_2[e]	C_2	0.14988	−348.05372		16.2	
cyclononatetraenyl anion	D_{9h}	C_2[e]	0.14214	−348.32828		41.0	

[a] The first column gives the symmetry of the singlet, and the second gives the symmetry of the triplet. [b] These energies are given in Hartrees. [c] Singlet−triplet gap. A negative value indicates that the triplet is more stable than the singlet. [d] CCSD(T) value, ref 110. [e] Möbius π-system, see text.

etry.[112] The calculated singlet−triplet gap is 77 kcal/mol (B3LYP/6-311+G*).

The singlet−triplet gaps are important quantities in characterizing these systems. In addition to the previously published calculations (see below), they have been calculated at the B3LYP/6-311+G* level and for the smaller molecules, also at the G2 level (Table 10), to provide a comparison with the data in Table 1. Here, the symmetries of the singlet and triplet states are given along with the triplet energies and the zero-point energies.

Cyclopropenyl anion adopts a C_{3v} geometry in the triplet state[113] and gives a calculated singlet−triplet gap of 13 kcal/mol. This small gap is characteristic of antiaromatic systems. The reason for the C_{3v} symmetry rather than D_{3h} in the triplet state is not clear.

Cyclopentadienyl cation has C_{2v} symmetry but adopts a D_{5h} symmetry in the triplet state. As expected for a $4n$ molecule, it has a small singlet−triplet gap, and here, the triplet state is calculated to have the lower energy,[110] in agreement with experimental observations.[72] In contrast, the aromatic cyclopentadienyl anion with D_{5h} symmetry has its symmetry reduced to C_s in the triplet state. Here, the singlet−triplet gap is 68 kcal/mol. This is similar to that for benzene.

The difference in singlet−triplet gap between cyclobutadiene and cyclopentadienyl cation is interesting. Borden showed that it results from the difference in symmetry.[68] With cyclobutadiene, the degenerate "nonbonding" π-MOs can be chosen so that they are associated with different pairs of atoms. Since in the singlet the two electrons in the NBMOs have opposite spin, it is possible for each of the electrons in the bonding π-MO to localize partially at the same pair of carbons as the nonbonding electron that has the same spin. This type of correlation between the electrons in the bonding and antibonding MOs is energetically advantageous. It is not possible in the triplet state because the electrons in the NBMOs have the same spin. As a result, the energy of the singlet drops below that of the triplet in square cyclobutadiene.

The NBMOs of cyclopentadienyl cation cannot be localized in this fashion, and as a result, the triplet lies below the singlet, in accord with Hund's rule.[114]

Cycloheptatrienyl cation has D_{7h} symmetry, which is reduced to C_2 in the triplet state. The calculated singlet−triplet gap is 73 kcal/mol, similar to that for benzene and cyclopentadienyl anion. The $4n$ anion has C_2 symmetry, and this is increased to D_{7h} in the triplet state.[110] The singlet−triplet gap is −2 kcal/mol, with the triplet having the lower energy.

Cyclononatetraenyl anion has D_{9h} symmetry, which is reduced to C_2 in the triplet state. However, this triplet is calculated to have a Möbius π-system which leads to some stabilization. Here, the calculated singlet−triplet gap is 41 kcal/mol, significantly smaller than for the other $4n + 2$ systems. As noted above, the cation with C_2 symmetry has a Möbius π-system[98] and the triplet has C_2 symmetry. The singlet−triplet gap is 16 kcal/mol.

Cyclooctatetraene has D_{2d} symmetry, which is increased to D_{8h} symmetry in the triplet state.[110] The calculated singlet−triplet gap is 16 kcal/mol at the 6-311+G* level or 24 kcal/mol at the CCSD(T) level, which may be compared with the experimental value of 25 kcal/mol.[110]

It can be seen that the expectations based on Baird's analysis are reproduced. The $4n + 2$ singlet states have reduced symmetry in the corresponding triplet states, and the singlet−triplet gaps are large. The $4n$ singlet states have their symmetry increased on going to the triplet states, and the singlet−triplet gap is small. The calculated NICS values are in agreement, with the $4n$ triplet states having shielding values.[110]

12. Origin of Aromaticity and Antiaromaticity

Aromaticity has been the subject of a large number of studies.[17] Some have proposed that it is the σ-system that makes benzene a regular hexagon and that the π-electrons would prefer a D_{3h} distorted structure,[115] and this view has received considerable support.[116] However, contrary opinions have been presented.[117] Many attempts have been made to separate the σ- and π-energies,[118] but the strong coupling between the σ- and π-systems via the electron repulsion terms makes this very difficult.

There appears to be one common requirement for aromatic character: a closed-shell conjugated π-system (i.e., no partially filled degenerate orbitals) where n π-electrons can be distributed over approximately

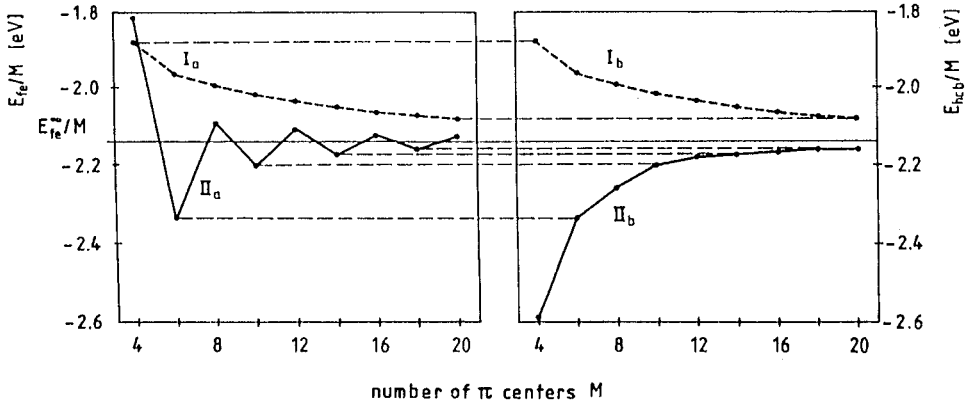


Figure 2. Results of calculations for conjugated polyenes. (Left) Results of full calculations, where the dashed line (Ia) gives the normalized π-energies for linear polyenes and the solid line (IIa) gives the energies for cyclic polyenes. The line at 2.14 eV represents the limit for an infinite chain. (Right) Results of calculations in which the antisymmetry principle was not included. The energies for the linear polyenes and the $4n + 2$ cyclic polyenes are unchanged, but the $4n$ cyclic polyenes are calculated to be too stable. (Reprinted with permission from ref 124a. Copyright 1996 Elsevier Science.)

Table 11. Electronic Transition Energies of Polyenes and Polymethinum Ions

	$Me_2N^+{=}CH{-}(CH{=}CH)_n{-}NMe_2$	$Me{-}CH{=}CH{-}(CH{=}CH)_n{-}Me$
n	λ_{max}[122]	λ_{max}[123]
1	310	225
2	412	272
3	510	310
4	660	341

n σ-bonds. Dewar and Schmeising[119] in 1959 pointed out that such an arrangement would reduce the repulsion of the paired π-electrons in a Kekule structure for benzene, thus contributing to stabilization. In effect, that is what we mean when we talk about a delocalized structure.[120] In this connection, it is useful to compare the linear conjugated polyenes and the polymethinium ions. With the former, there is little evidence for significant stabilization and the lowest energy electronic transition moves to the red only slowly with increasing number of double bonds. The polymethinium ions have two equivalent 'resonance' structures, which implies that they have essentially one π-electron per σ-bond.

$$Me_2N^+{=}CH{-}(CH{=}CH)_n{-}NMe_2 \leftrightarrow Me_2N{-}(CH{=}CH)_n{-}CH{=}N^+Me_2$$

Here, the bond lengths become approximately equal and the lowest energy electronic transition moves rapidly toward the red with increasing number of double bonds (Table 11) whereas the shift is much smaller with the linear polyenes that have fixed single and double bonds. The location of the ions electronic transitions may be estimated using a particle in a box model,[121] just as that for benzene may be estimated using a particle on a circle model. The π-electron systems in these ions are closely related to those in the aromatic systems.

The origin of antiaromaticity is less clear. The $4n$ π-electron systems become antiaromatic when they are required to be planar, thus forcing the interaction of the π-orbitals. The antiaromaticity may be reduced when the molecule may become nonplanar (such as cyclopropenyl anion and cyclooctatetraene). In what way does the interaction of the π-electrons lead to destabilization?

Böhm and Schütt[124] presented quantum Monte Carlo calculations for the π-systems of these compounds. Electronic degrees of freedom are restricted by two quantum constrains. The first is the Pauli antisymmetry principle (PAP) which requires that many electron wave functions must change sign when the ordering of two electrons with the same spin is changed. The second is the Pauli exclusion principle (PEP) that prevents conformations with more than one electron of the same spin in the same atomic orbital. They carried out two sets of calculations. First, the Pauli exclusion principle was retained but the Pauli antisymmetry principle was not required, and in the second both principles were applied.

The result of their calculations are shown in Figure 2. The upper left plot gives the normalized π-energies (E_π/M = number of π-centers) for a linear polyene (dashed line) and for a cyclic polyene (solid line). The line at 2.14 eV is the extrapolated value for an infinite chain. In accord with expectations, the highest normalized energy is found for $M = 4$ (cyclobutadiene), and for the other cyclic polyenes, the normalized energies are more negative than for a linear polyene. The $4n + 2$ systems are stabilized with respect to an infinite chain and the $4n$ systems are destabilized. This is, of course, what is found in all calculations.

These results may be compared with those at the upper right, where the antisymmetry principle was not included in the calculations. Here, the normalized π-energies change smoothly with increasing number of p centers. The values for the open-chain polyenes and for the $4n + 2$ cyclic polyenes are the same as those for the full calculations. However, the full calculation for the $4n$ cyclic polyenes gives higher π-energies than those found in the right-hand plot. Thus, they concluded that the antisymmetry principle is a 'hidden variable' in the π-electron calculations and that it is responsible for the destabilization of the $4n$ π-electron systems.

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