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Antiaromaticity in Open-Shell Cyclopropenyl to Cycloheptatrienyl Cations, Anions, Free Radicals, and Radical Ions

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I. Introduction

The concept of antiaromaticity in cyclic conjugated organic molecules was introduced by Breslow,[1] who proposed there are magnetic, spectroscopic, and thermodynamic criteria for defining this elusive property. Even more than for aromaticity,[2] the definition of antiaromaticity is inexact and controversial but the concept is also very useful and has attracted continued attention. While the existence of antiaromaticity as a phenomenon with demonstrable major effects in chemical systems has been repeatedly and convincingly demonstrated, denials and refutations of such effects are also common. Many different methods and criteria have been applied to the study of aromaticity and antiaromaticity, and those given

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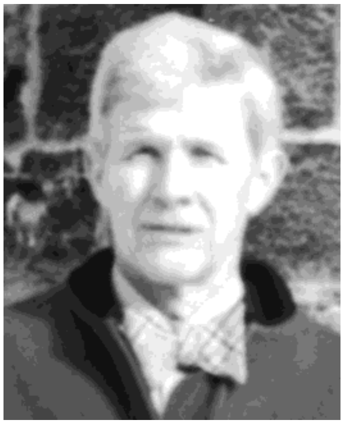

Thomas T. Tidwell was born in Atlanta, GA, in 1939 and received his B.S. degree at the Georgia Institute of Technology and his Ph.D. degree at Harvard University in 1964, where he worked on steric crowding under the direction of Professor P. D. Barlett. He carried out postdoctoral work at the University of California, San Diego, with Teddy Traylor, and at the University of East Anglia (U.K.) with Alan Katritzky. Since 1972 he has been at the University of Toronto, where he is Professor of Chemistry. His research interests involve the reactive intermediates of organic chemistry, including ketenes and carbocations. He is currently Vice-President of the IUPAC Division of Organic and Biomolecular Chemistry, and as a hobby he pursues the history of organic chemistry, in which field he recently published an essay on Wilhelm Schlenk (*Angew. Chem., Int. Ed.* **2001**, *40*, 331–337).

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Table 1. Criteria for Aromaticity and Antiaromaticity (for neutral even-electron singlet species)[2c]

property	aromatic	olefinic	antiaromatic
(i) electronic nature			
	(4n+2) π-electron cyclic conjugation	no cyclic conjugation	4n π-electron cyclic conjugation
(ii) energy			
cyclic conjugation	stabilization	standard	destabilization
delocalization	enhanced	standard	decreased
HOMO−LUMO gap	larger	standard	smaller
(iii) geometry			
bond lengths	equalization	alternation	alternation
(vi) magnetic properties[5,6]			
diamagnetic anisotropy	enlarged		small
susceptibility exaltation	large		low
^{1}H NMR shifts	diatropic (low field)		paratropic (high field)
NICS	large negative		large positive
(v) reactivity			
chemical structure	e.g., benzene	e.g., cyclohexadiene	e.g., cyclooctatetraene
retention of structure	electrophilic substit.	electrophilic addition	addition
(vi) spectroscopy			
UV spectra	high energy	standard	low energy
IR/Raman spectra	large symmetry		low symmetry

by Breslow have been considerably elaborated, as recently summarized in Table 1.[2c] These criteria were intended for neutral even-electron singlet species and do not always apply to the wider range of structures considered here.

This article is concerned with cationic, anionic, and free radical conjugated cyclic hydrocarbons that do not contain the Hückel $4n + 2$ number of π-electrons. Thus, among species with no more than one charge, there are the 3, 4, 5, 7, and 8 π-electron structures **1**−**10** for monocyclic rings up to seven-membered.

The extension of the concept of aromaticity (and hence of antiaromaticity) to the odd-electron systems **1**, **3**, **4**, **6**, **7**, **8**, and **9** may be considered questionable, as the first criterion listed in Table 1 for aromaticity is the presence of $(4n + 2)$ π-electron cyclic conjugation and correspondingly for antiaromaticity $4n$ π-electron cyclic conjugation, thus not including odd-electron systems. However, the second criterion in Table 1 refers to whether cyclic conjugation stabilizes or destabilizes a system, and this criterion is independent of whether there is an odd number of electrons. Similarly, geometric criteria and others may be applied to odd-electron systems. In practice, the question of aromatic or antiaromatic character of odd-electron systems has been asked by some authors but not by others. Aromaticity in neutral free radicals and radical ions was considered explicitly by Vincow in 1971,[2e] although the discussion focused on the cycloheptatrienyl radical **9**. A related question involves triplet states of even-electron systems, for as pointed out by Baird in 1972[3a] and elaborated by Schleyer et al.,[3b] aromatic versus antiaromatic character may be reversed between singlet and triplet species, as indicated by energetic, magnetic, and geometric criteria. As noted below, these studies were extended to the odd-electron cyclopentadienyl radical.[3b] Recent calculations of the energy levels of the benzene radical cation **7** and anion **8** have been proposed to confirm the antiaromatic character of these species.[3c]

The induced π-electron ring currents and relative diamagnetic susceptibilities of the cyclic hydrocarbon species C_3H_2, $C_4H_3^+$, C_5H_4, $C_6H_5^+$, and C_7H_6 were interpreted in terms of possible antiaromatic character in singlets and triplets.[3d,e] These species may have carbenic character and odd numbers of π electrons.

For a number of the systems considered below, the question of aromaticity/antiaromaticity has yet to be critically examined, and data to consider the application of many of the criteria of Table 1 are not available. In these cases, reference is made to preparative work and to the properties for these species as far as they are known in the hope that this may stimulate further examination of these interesting molecules.

In addition to the magnetic, spectroscopic, and thermodynamic criteria for antiaromaticity outlined by Breslow,[1] geometric effects are commonly considered, in that aromaticity favors bond equalization while antiaromaticity leads to bond alternation. A characteristic of antiaromatic systems that is not explicitly noted in Table 1 is the occurrence of degenerate structural isomerism of a series of equivalent nonsymmetrical structures. For odd-electron systems, this is caused by Jahn−Teller[4a] distortion in which geometrical change occurs to prevent unequal occupancy of degenerate orbitals, and this also occurs in 4π- and 8π-electron systems. These distorted structures are lower in energy than the fully conjugated symmetrical structures, although the energy differences may not be large. Another geometric consideration relevant to aromaticity criteria is the proposal of Hiberty and Shaik[4b] that for benzene the equalization of bond lengths is primarily enforced by the σ-bonds, whereas the π-electron system favors alternating bond lengths. This proposal has received considerable attention but does not appear to have been applied to the consideration of antiaromaticity.

Magnetic effects result from aromatic diatropic and paratropic antiaromatic ring currents and are reflected in ^{1}H NMR chemical shifts, magnetic susceptibility exalation,[5] and nucleus-independent chemical shifts.[6] Magnetic susceptibility exaltations (λ)[5] are derived from magnetic susceptibilities χ which may be calculated by the IGLO method.[7] The exaltations are obtained from the differences between χ_{tot} and nonaromatic values derived from increments for hypothetical polyene systems without cyclic delocalization.

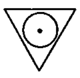
Nucleus-independent chemical shifts (NICS)[6] provide a useful criterion of aromaticity/antiaromaticity. Absolute magnetic shieldings are computed at ring centers (nonweighted mean of the heavy atom coordinates) and correspond to the NMR chemical shift convention the signs are reversed, so that negative NICS values denote aromaticity and positive NICS values denote antiaromaticity.

Other theoretical treatments which have been applied to considerations of antiaromaticity include spin-coupled theory,[8a] topological methods,[8b,c] and quantum statistical definitions.[8d] The relevance of spin-coupled theory has been described: "The comparison between the (spin-coupled) descriptions of cyclobutadiene, benzene, and cyclooctatetraene clearly indicates that the reason for the lower stability and higher reactivity of antiaromatic systems is due to a simultaneous unfavorable coupling of the spins of all valence orbitals to triplet pairs, which discourages bonding interactions and suggests diradical character."[8a]

Topological resonance energies are Dewar resonance energies comparing cyclic systems to acyclic polyenes within the Hückel scheme and have been reported for **1**−**10** as shown in Table 2.[8c] Negative values (in β units) indicate reduced conjugative stability relative to acylic models, and this criterion indicates destabilization in all these species. These values are not normalized for different numbers of electrons.

Reactivity was an early criterion for aromaticity and was one of the first applied in studies of antiaromaticity.[1] This includes both qualitative and quantitative studies of reactivity in forming or destroying antiaromatic systems, for example, in the resistance to forming systems such as cyclobutadiene, and their high chemical reactivity if made.

The discussion of antiaromaticity has been rather episodic, and the current review will attempt to summarize the major studies on each of the structures **1**−**10**. This approach serves to highlight gaps in current knowledge, particularly involving odd-electron systems.



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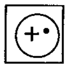

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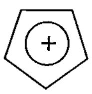

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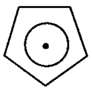

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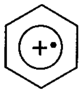

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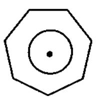

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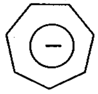

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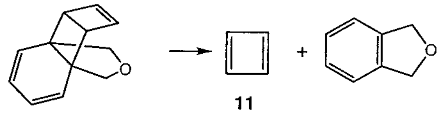
Table 2. Topological Resonance Energies[8c]

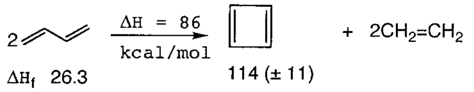
compound	TRE	compound	TRE
1	−0.464	**6**	−0.301
2	−1.464	**7**	−0.300
3	−0.461	**8**	−0.210
4	−0.461	**9**	−0.220
5	−0.919	**10**	−0.665

II. Cyclobutadiene

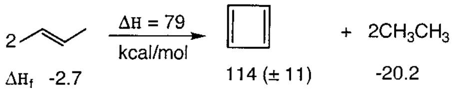
Cyclobutadiene (**11**) is the epitome of an antiaromatic neutral hydrocarbon and has been the target of chemical investigations for well over a century,[9a] with much early interest stimulated by the studies of Willstätter.[9b] This compound serves as a benchmark for extreme manifestations of antiaromaticity. A recent experimental measurement by photoacoustic calorimetry of the energy change in the formation of cyclobutadiene shown in eq 1 permits derivation of ΔH_f for **11** of 114 ± 11 kcal/mol.[9c] The destabilization relative to a hypothetical unstrained conjugated polymer consisting of four CH units is 87 ± 11 kcal/mol, of which 32 ± 2 kcal/mol is due to strain and 55 ± 11 kcal/mol is due to antiaromatic destabilization. Essentially the same value is derived from the homodesmotic comparison for eq 2 based on the experimental $\Delta H_f°$ value. The isodesmic calculation of eq 3 gives a total destabilization of 79 kcal/mol, with an antiaromatic destabilization of 48 ± 11 kcal/mol.



(1)



(2)



(3)

Thus, the cyclobutadienyl 4π-electron system is remarkably destabilized by antiaromaticity, and as noted below, the same situation holds for the 4π-electron cyclopropenyl anion **2**, cyclobutenone enolate **19a**, and cyclopentadienyl cation **5**. Larger and odd-electron systems suffer less destabilization, as do systems which can reduce antiaromaticity by pyramidalization or electron delocalization into fused benzene rings.

III. Cyclopropenyl Radical

The cyclopropenyl radical **1** has been studied experimentally[10] and theoretically.[11] Experimentally, cyclopropenyl radical is determined by ESR to have C_s symmetry with a pyramidalized carbon. The structure of the cyclopropenyl radical has been calculated by Glukhovtsev et al.[11a] and by Merrill and Kass,[11i] and the C−H bond angle at the radical center

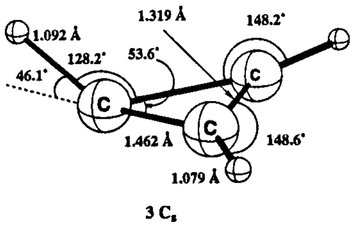


Figure 1. Structure of the cyclopropenyl radical **1** calculated at the MP2(full)/6-31G(d) level. (Reprinted with permission from ref 11a. Copyright 1996 American Chemical Society.)

is calculated to be bent 46.1° from the plane of the three carbons (Figure 1).

The difference between the experimental heat of formation of **1** of 105.2 ± 4.1 kcal/mol and the calculated value of 116.5 kcal/mol led to the suggestion that the experimental value may need revision.[11a]

(4)

1

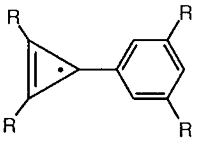
The G2 calculated reaction enthalpy derived by eq 4 for the cyclopropenyl radical is only 8.9 kcal/mol compared to values of 59.1 and −4.3 kcal/mol for the comparable reactions of the cyclopropenyl cation and anion (eq 5), and the much lower stabilization of the radical compared to the cation was interpreted[11a] as indicating that the cyclopropenyl radical is not aromatic. The large differences between the three

(5)

2

give a powerful example of the effects of the number of electrons on the stability of cyclic conjugated systems, and the fact that the energy change for the radical more closely resembles the anion suggests that the radical shares to some degree the antiaromatic destabilization of the anion.

The arylcyclopropenyl radical **12** had larger hyperfine splittings of the ring hydrogens than did the allyl radical **13** or the benzyl radical **14**. From these results it was concluded there was greater delocalization of the radical into the aryl group for **12** than in **13** or **14**, and this was taken as evidence for antiaromatic destabilization of the cyclopropenyl radical that induced electron delocalization into the phenyl ring.[10c]



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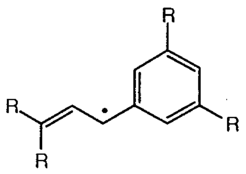

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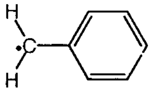

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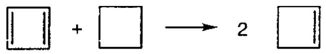
Calculations using the complete basis set ab initio method for the cyclopropenyl radical give an ionization energy of 6.17 eV, in good agreement with an experimental energy of 6.60 eV, and an electron affinity of 0.45 eV.[11k] The very low value of the former is indicative of the large aromatic stabilization of the cation, and the low value of the latter indicates the instability of the cyclopropenyl anion. The radical is intermediate between the two, but these results do not permit an estimate of any antiaromatic destabilization of the radical.

IV. Cyclopropenyl Anion and Analogues

A. Cyclopropenyl Anion

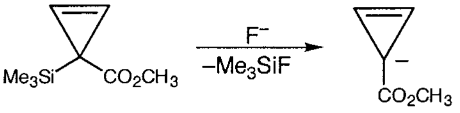
The stabilization energy of the cyclopropenyl anion **2**[12] calculated for the homodesmotic reaction of eq 5 is negative,[11a] but the value of −4.3 kcal/mol is far less in magnitude than the destabilization of −31.0 kcal/mol for cyclobutadiene (eq 6). However, this



(6)

provides no evidence for stabilization of **2** by conjugation. A pyramidal structure is calculated for **2**, and this serves to minimize the electron−electron repulsion and thereby substantially reduces the destabilization of a fully conjugated system.[11a,i] Substituted cyclopropenyl anions were also studied by calculations.[11i] Experimental determinations using reduction of cations by cyclic voltammetry gave pK_a values for triphenyl-, trimethyl-, tri-*n*-propyl-, and tri-*tert*-butylcyclopropenes of 50, 62, 64, and 65, respectively.[11j] These very large values are indicative of the great destabilization of **2** and substituted derivatives.

The cyclopropenyl anion **15** was obtained in the gas phase by the reaction of eq 7, with ΔH_{acid} of the conjugate acid of 391 ± 4 kcal/mol,[12b] and an experimental destabilization of 14 kcal/mol was found by the reaction of eq 8.[11i] The cyclopropenyl anion **16** was long-lived in solution and detected by UV (eq 9).[12c]



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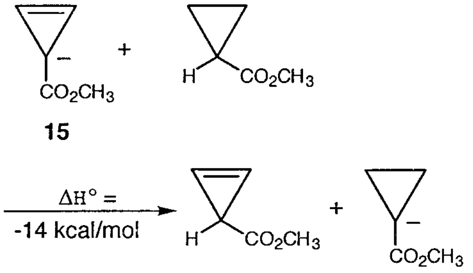

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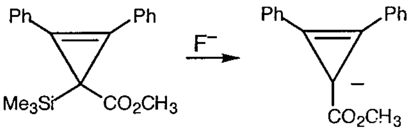

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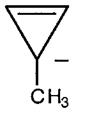
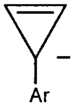
(9)

The methyl anion **15a** could not be prepared by analogous desilylation procedures, and ring opening occurred instead.[12d] Calculations gave values of $\Delta H_{acid}°$ for 3-methylcyclopropene[12d] and 3-phenylcyclopropene[12e] of 415.5 and 398.1 kcal/mol, respectively, and an experimental value of 398.6 ± 1.4 kcal/mol for 3-(4-methylphenyl)cyclopropene leading to **15b** was obtained by a kinetic method.[12e] Aryl anions such as **15b** rearrange to indenyl anions and could not be studied directly.[12e]

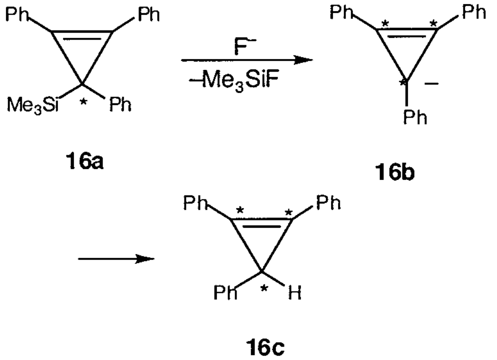


15a



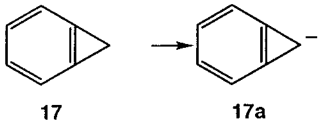
15b (Ar = 4-$CH_3C_6H_4$)

Fluorodesilylation of **16a** specifically labeled with ^{13}C gave the anion **16b** which was protonated to give **16c** with a nearly statistical distribution of the ^{13}C label.[12f] This was interpreted as showing the formation of **16b** as a nonplanar singlet which equilibrated the carbons by pseudorotation before capture by a proton.[12f] The anion **16b** was reported[12e] to be generated in the gas phase by the same reaction, and the conjugate acid has $\Delta H_{acid}°$ of 385± 5 kcal/mol,[12g] but following a reinvestigation it was suggested that **16b** rearranges in the gas phase to a 1,2-diphenyl-1-indenyl anion.[12e]



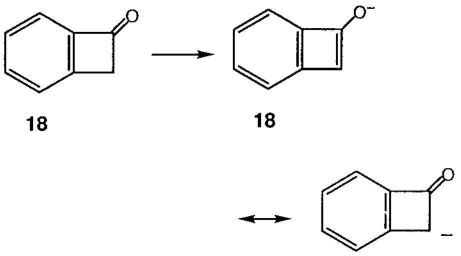
B. Benzocyclopropenyl Anion and Benzocyclobutenone Enolate

Deprotonation of benzocyclopropene (**17**) gave the benzocyclopropenyl anion (**17a**)[13a] in the gas phase (eq 10), and the measured acidity $\Delta H°_{acid}$ of 386 ± 3 kcal/mol was 34.5 kcal/mol more favorable than for the allylic position of cyclopropene. The greater



(10)

acidity of **17** was attributed to alleviation of the unfavorable 4π-electron destabilization in the anion by the benzene ring and pyramidalization at the anionic center in **17a**, which minimizes conjugation of the lone pair.[13a] The benzocyclobutenone enolate (**18**) was formed by deprotonation of benzocyclobutenone in the gas phase (eq 11) and was also generated and trapped in solution.[13b] The gas-phase $\Delta H°_{acid}$ was 360.3 ± 2.1 kcal/mol, which is 10 kcal/mol less favorable than for the model 1-phenylpropan-2-one. However, destabilization of **18** due to the antiaromatic cyclobutadiene character of the enolate was reported to be avoided by delocalization of negative charge to the benzene ring and to oxygen. Cyclobutenone (**19**) is calculated to be 22 kcal/mol less acidic than benzocyclobutenone (eq 12), and this is ascribed to cyclobutadiene destabilization in **19a**.[13b]



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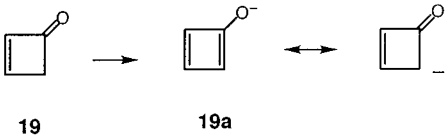

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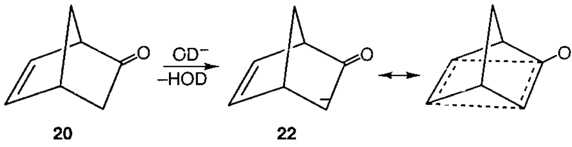
C. Homoantiaromaticity in 4π-Electron Carbanions

The concept of homoantiaromaticity has been considered in proton abstraction from the norbornenyl systems **20**[14a] and **21**[14b,c] forming the carbanions **22** and **23** (eqs 13 and 14). Most notably, the rate constants for base-catalyzed hydrogen exchange for deuterium in **20** were diminished relative to the corresponding rate constants for norcamphor by factors of 75 (*exo*) and 13 (*endo*), a result attributed to possible 4π-electron antiaromatic destabilization in **22**.[14a] Lesser effects were obtained for **21.**[14b,c] Calculations for **23** gave homodesmotic comparisons and gas-phase proton affinities which provide no evidence for bis-homoantiaromaticity, and the ion was found to be stabilized by delocalization of the negative charge into antiparallel C–C bonds giving lengthened σ bonds.[14d] Recent computational studies confirm the lower acidity of **20** compared to norcamphor,[14e] and the cause of this effect merits further study.



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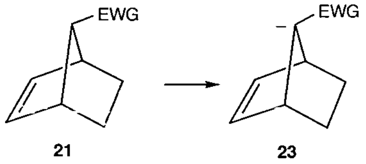


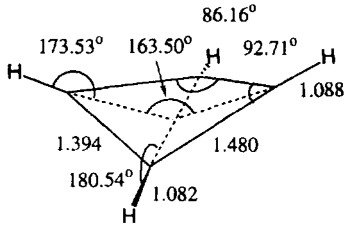
EWG = CN,[14b] CO_2CH_3[14c]

(14)

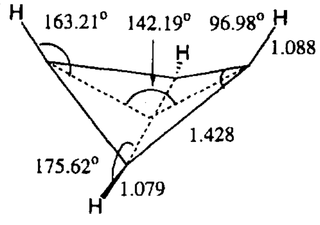
V. Cyclobutadienyl Radical Ions

A. Cyclobutadienyl Radial Cation

Recent theoretical studies of the cyclobutadienyl radical cation **3** have appeared,[15a] including the



puckered parallelogram
C_2, saddle point



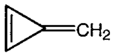
puckered rhombus
C_{2v}, minimum

Figure 2. Calculated geometries of Jahn–Teller-distorted structures of cyclobutadiene radical cation. (Reprinted with permission from ref 15i. Copyright 1995 Elsevier Science.)

formation from ionized tetrahedrane[15b] from the reaction of acetylene with acetylene radical cation[15c] and from ionized naphthalene.[15d] A square nearly planar structure for **3** was initially calculated by MNDO,[15e] while more advanced calculations show two Jahn–Teller-distorted states for **3** (Figure 2) which are very close in energy.[15i] Experimental studies indicate that **3** is less stable than the radical cations of vinylacetylene **24a** and methylenecyclopropene **24b** by 2.2 and 6.9 kcal/mol, respectively.[15f,g]

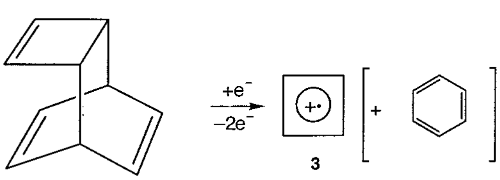
$CH_2{=}CHC{\equiv}CH$

24a



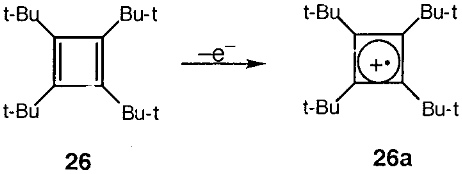
24b

Experimentally, **3** was produced in the gas phase as detected by the 70-eV electron-ionization mass spectrum of Nenitezscu's hydrocarbon (**25**) and its benzo-analogues (eq 15).[15f,g]



25 (15)

Oxidation of tetra-*tert*-butylcyclobutadiene (**26**) or tetra-*tert*-butyltetrahedrane by $AlCl_3$[15e] or electrochemically[16a] produces the radical cation **26a** (eq 16). Photolysis of adamantyl-substituted alkynes in the presence of $AlCl_3$ produces adamantyl-substituted analogues of **26a** whose ESR spectra were recorded.[16b]



26 **26a** (16)

In-plane delocalized 4C/3e radical cations have been generated by one-electron oxidation of the corresponding dienes (Figure 3).[16c] The corresponding dications are cited as σ-bishomoaromatic 4C/2e dications, and the lower oxidation potential of the diene shown (0.84 V) compared to the corrsponding monoene (1.46 V) is taken as evidence of stabilization of the radical cation by 4C/3e in-plane delocalization.[16c]

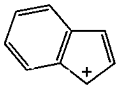
B. Cyclobutadienyl Radical Anion

There is little information available concerning the cyclobutadienyl radical anion **4**. Experimental evidence was obtained for the radiolytic formation of the acetylene radical anion in HZSM5 zeolite, and the structure and energy of **4**, which is a possible product from this reaction, was calculated using DFT methods.[15a] A rectangular planar structure was found with CC bond lengths of 1.519 and 1.400 Å, as compared to values of 1.509 and 1.381 Å calculated for the radical cation **3**.[15a] Linear butatriene structures $CH_2{=}C{=}C{=}CH_2^{\bullet -}$ were calculated to be lower in energy than **4** by 37–38 kcal/mol.

VI. Cyclopentadienyl and Homocyclopentadienyl Cations

A. Cyclopentadienyl Cations

The cyclopentadienyl cation (**5**) and its mono- and dibenzannelated analogues the indenyl (**27**) and fluorenyl (**28**) carbocations have been the subject of frequent study. In 1925, Ziegler and Schnell[17a] reacted pentaphenylcyclopentadienol (**29**) with concentrated H_2SO_4 and upon hydrolysis obtained products derived from the cation **30** (eq 17). Later studies[17b,c] showed the cation **30** is long-lived below −40 °C, and this was characterized by UV and ESR and shown to have a low-lying excited triplet state.[17c] The pentachlorocyclopentadienyl cation **31** was shown to be a ground-state triplet.[17c] The study of such ground-state triplets has been pursued because of possible applications as ferromagnets.[17d]



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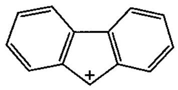

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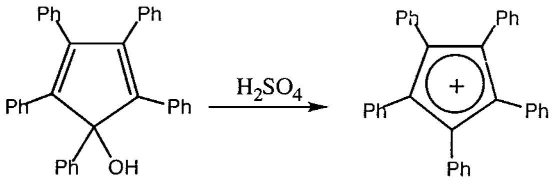


29 **30** (17)

In an attempt to generate the cyclopentadienyl cation **5**, cyclopentadienyl iodide (**32**) was treated with silver perchlorate. However, in propionic acid at −15 °C, **32** was inert to these conditions (eq 18)[17e] but by contrast was 10 times more reactive toward

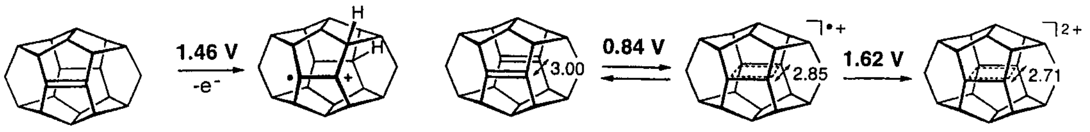


Figure 3. Formation of a 4C/3e in-plane delocalized radical cation. (Reprinted with permission from ref 16c. Copyright 2000 Elsevier Science.)

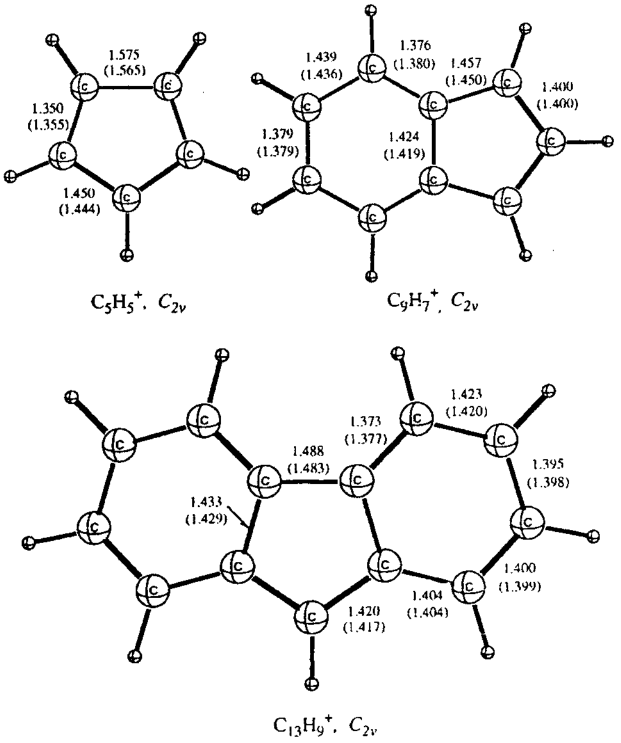
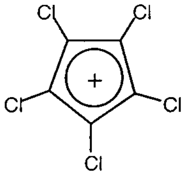
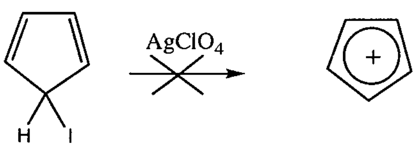


Figure 4. B3LYP/6-31G* and MP2/6-31G* (in parentheses) calculated geometries of singlet cyclopentadienyl (**5**), indenyl (**27**), and fluorenyl (**28**) cations. (Reprinted with permission from ref 19a. Copyright 1997 American Chemical Society.)

bromide ion than is cyclopentyl iodide.[17i] This may indicate cyclopentadienyl iodide reacts with bromide by an S_N2-type process with cyclopentadienyl anion character in the transition state.[17i]



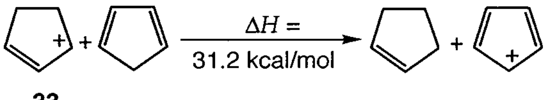
31



32 **5** (18)

Electrochemical oxidation of the cyclopentadienyl anion also did not yield **5** and led to an estimate that the p$K_R{}^+$ of **5** was −40 or lower, which is 20 units lower than values for representative conjugated allylic cations.[17f]

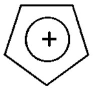
The gas-phase ionization potentials of the cyclopentenyl and cyclopentadienyl radicals were measured and provide hydride affinities of the corresponding cations, which lead to a calculated ΔH of 31.2 kcal/mol for the reaction of eq 19.[17g] This



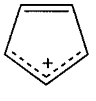
33 **5** (19)

thermodynamic criterion produces a quantitative measurement of the enormous destabilization of the cyclopentadienyl cation **5** compared to the cyclopentenyl cation **33**, which is highly stabilized by delocalization. This result shows the very large energetic penalty due to antiaromaticity. The gas-phase ionization potential of the cylopentadienyl radical is 8.69 eV, and this high value also reflects the instability of the cation.[17l]

The cyclopentadienyl cation (**5**) was generated in a matrix and observed by ESR spectroscopy.[18a] Simple Hückel theory predicts this species will have a triplet ground state with a symmetrical D_{5h} geometry **5a**, and this is confirmed by recent ab initio calculations;[18c] the ESR spectrum of **5** in a matrix is in agreement with the triplet ground state.[18a,b] The calculations indicate the C_{2v} singlet structure **5b** with a planar *cis*-butadienyl moiety is 8.7 kcal/mol higher in energy than the triplet.[18c−e] The B3LYP/6-31G* calculated structures[19a] of the singlet and triplet cyclopentadienyl, indenyl, and cyclopentadienyl cations are shown in Figures 4 and 5.



5a



5b

The IR spectrum of the pentachlorocyclopentadienyl cation $C_5Cl_5{}^+$ (**31**) has been measured in an SbF_5 matrix,[17h] and this cation is determined to have D_{5h} symmetry by DFT calculations.[17h] Substituted cyclopentadienyl cations in the gas-phase undergo carbon skeletal rearrangements and loss of alkyne units that can be explained by the formation of carbocations with a square pyramidal structure (Figure 6).[17j,k] This structure[20] was initially estimated to be more stable than planar structures,[18d] but later calculations confirm the latter are more stable.[18c,e] Cyclopentadienyl cations with several strongly electron-donating substituents have been obtained as stable salts.[18f]

The calculated magnetic susceptiblity exaltation (λ) and nucleus-independent chemical shift of the singlet cyclopentadienyl cation of 32.6 (ppm cgs) and 54.1, respectively, both indicate strong antiaromatic effects in this cation.[19a] The triplet is found to be more stable

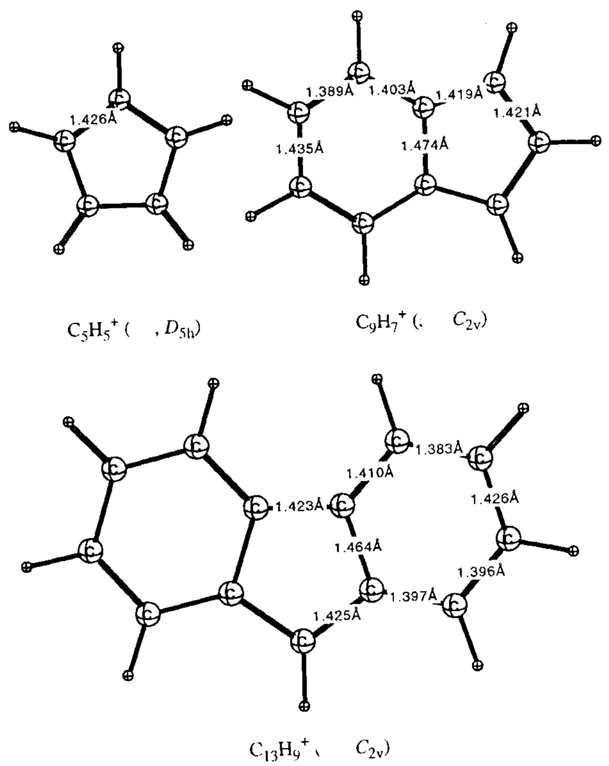


Figure 5. B3LYP/6-31G* calculated geometries of triplet cyclopentadienyl (**5**), indenyl (**27**), and fluorenyl (**28**) cations. (Reprinted with permission from ref 19a. Copyright 1997 American Chemical Society.)

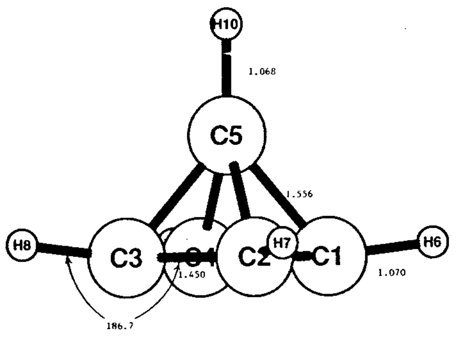
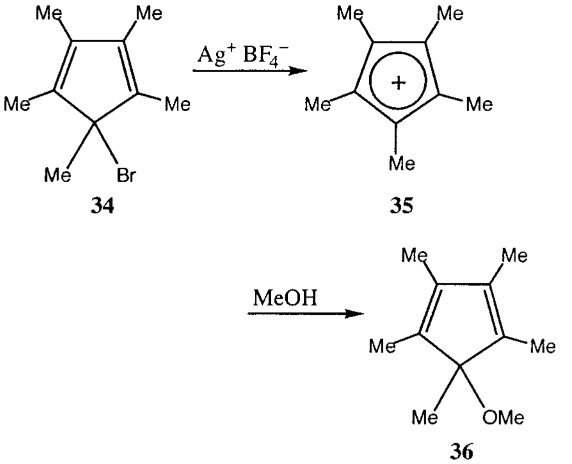


Figure 6. Square pyramidal structure of the cyclopentadienyl cation. (Reprinted with permission from ref 18d. Copyright 1989 American Chemical Society.)

than the singlet by 10.5 kcal/mol (B3LYP) and 7.6 kcal/mol (CCSD(T)/CC-pVDZ).[3b] Comparative calculations at the HF/6-31+G* level give comparative values of λ as 30.5 for the singlet and -3.3 for the triplet and for NICS 49.2 for the singlet and -4.5 for the triplet, both indicating aromatic character for the D_{5h} triplet.[3b] The C−C bond length in the triplet is 1.426 Å, near that of benzene, while the singlet shows an alternation of 0.228 Å in the bond lengths.[19a] The cyclic destabilization of **5** as determined by the calculated homodesmotic reaction energy fits a correlation with the differences in calculated ^1H shielding of fully conjugated and monoene systems using **5** and cyclopentenyl cation.[19b] The energies and structures of a variety of alkyl-substituted cyclopentadienyl cations have been calculated using different levels of theory, and a methyl rearrangement of *tert*-butylcyclopentadienyl cation to a cationic structure analogous to **38d** (vide infra) was determined.[19c]

Generation of cyclopentadienyl cations by solvolysis has been reported,[21] and the reactions of pentamethylcyclopentadienyl bromide (**34**) with $AgBF_4$ in CH_2Cl_2 resulted in capture by nucleophiles including methanol and methylamine which could involve a cation **35** leading to the substitution products **36** (eq 20).[21a] Reaction of pentaarylcyclopentadienyl bromides with silver carboxylates gave mixtures of esters through similar cations.[21b]



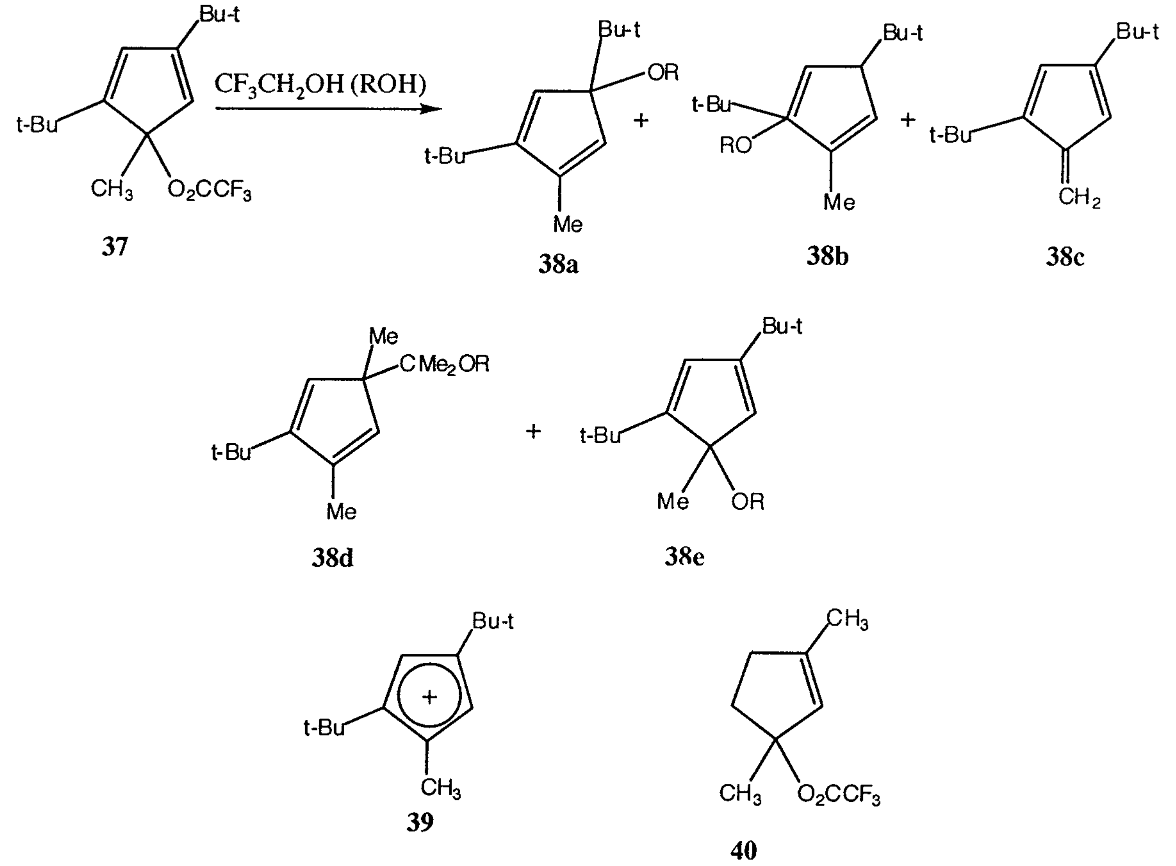
(20)

Solvolysis of **37** in trifluoroethanol gave a mixture of products **38a**,**b**,**e** from substitution with allylic arrangements, Wagner−Meerwein rearrangement product **38d**, and elimination product **38c** (Scheme 1).[21c] These are typical products characteristic of formation of a carbocation intermediate **39**. The reactivity of **37** showed a strong dependence on the solvent ionizing power parameter Y_{OTFA} with a value of the slope $m = 0.97$, and this is also diagnostic of a carbocation intermediate. The rate constant for solvolysis of **37** in CF_3CH_2OH is calculated to be less than that of 1,3-dimethyl-3-cyclopentenyl trifluoroacetate **40** by a factor of 10^{14}, showing the large kinetic effect of the antiaromatic destabilization of the cyclopentadienyl cation. The 5-phenyl-5-cyclopentadienyl trifluoroacetate corresponding to **37** also showed strong antiaromatic destabilization and was even less reactive than **37**, a result attributed to the presence of a twisted phenyl group which was less stabilizing than CH_3.[21c]

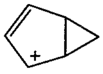
B. Homocyclopentadienyl Cations[22]

On the basis of initial ^1H NMR studies[22e] and theoretical calculations,[22b] the bicyclo[3.1.0]hexenyl cation **41** was described as a potentially homoantiaromatic species that possessed the cyclic conjugated 4π-electron system represented by **41a**. However, later theoretical studies of **41**[22c,d] and experimental studies of long-lived ions including **41**,[22e,f] the cyclohexadienyl cation **41c**,[22g] and methylated derivatives such as **41b**[22h−j] were interpreted as indicating the ion was nonaromatic. The allylic ion **41** was reported to be stabilized by electron donation from the two external C−C bonds of the cyclopropyl group and not the C_1−C_3 bond.[22d] A related example

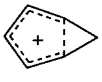
Scheme 1



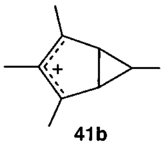
was reported,[22o] and homoaromaticity has been reviewed.[22p]



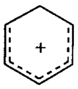
41



41a

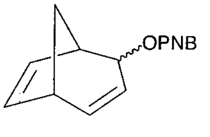


41b

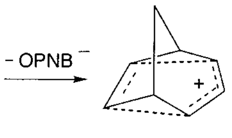


41c

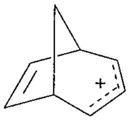
The rate constants for solvolysis of the *exo*- and *endo*-bicyclo[3.2.1]octa-2,6-dienyl *p*-nitrobenzoates **42a** with C−O bond cleavage were 230 and 240 times slower, respectively, than those of the corresponding monoenes **42b**.[22k,l] These rate retardations were



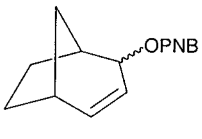
42a



43a



43b



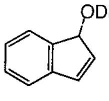
42b

interpreted as probably reflecting destabilization of the developing cation both by the antiaromatic bishomocyclopentadienyl cation character of **43a** and of inductive electron withdrawal by the double bond in allylic cation **43b**.[22k,l] Calculations of the structure of **43**, especially the paramagnetic susceptibilty exaltation Λ_{tot} of +8.1, confirm the bishomoantiaromatic character.[22m,n]

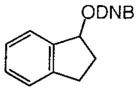
VII. Indenyl Cations

The indenyl cation **27** has not been directly observed by NMR, but the ^{1}H NMR spectra of ions substituted in the five-membered ring were interpreted as indicating charge was delocalized to all three carbons, and this was suggested to indicate that the ion did not have allylic character.[23a]

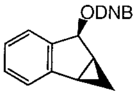
The solvolysis rate constant of 3-indenyl 3,5-dinitrobenzoate **44a** was 10^7 less than that of cyclopentenyl dinitrobenzoate **44d** and 5 × 10^5 less than that of indanyl dinitrobenzoate **44b**.[23b] Methoxy and methyl substituents at the 6-position on the ring in **44a** and a methyl substituent at the 1-position on the double bond have accelerating effects expected for benzylic and allylic stabilization, respectively.[23c] The cyclopropanated system **44c** showed no enhancement of reactivity compared to **44b**, and this was taken as evidence for a diminuation in reactivity for **44c** by a factor of 10^3 from that expected for a fully conjugating cyclopropyl group.[23d] The rate retardation was ascribed to due to homoantiaromaticity, of the type depicted for **41a**.



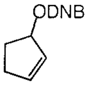
44a



44b

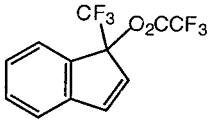


44c



44d

Solvolytic studies of the 3-trifluoromethyl derivative **45** indicated a diminution in reactivity of 10^9 relative to a 1-indanyl analogue comparable to **44b**, and factors of 10^6 and 10^3 were attributed to antiaromatic destabilization and to the rate retarding effect of the electron withdrawing CF_3 group, respectively.[24a]



45

A numerical scale of calculated values for antiaromaticity was derived from values of the HOMO–LUMO gap for different cations for which a value of 0 indicates no antiaromatic destabilization and with a maximum value of 1.0 for the cyclopentadienyl cation. On this scale of antiaromaticity, the value for the indenyl cation is 0.47 and that for the 9-fluorenyl cation is 0.33.[24b]

Comparative computational studies of the magnetic susceptibilities and nucleus-independent chemical shifts of cyclopentadienyl (**5**), indenyl (**27**), and fluorenyl (**28**) cations together with those of the corresponding anions are highly revealing of the nature of the antiaromatic effects in these species (Table 3). The same differences for more positive magnetic susceptibilities of the cations relative to the anions occur as benzene rings are incorporated, while the positive NICS values are strongly indicative of antiaromaticity for the five-membered rings of all three cations, while the six-membered ring for the indenyl cation is also antiaromatic, and even those of fluorenyl cation show much less aromaticity than those of the corresponding anions (−12.5 and −12.4, respectively) or of benzene (−11.5). Thus, by some criteria fluorenyl cation is nonaromatic, while by others there is appreciable residual antiaromaticity.

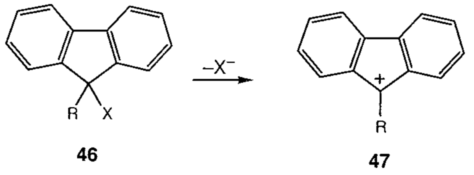
Table 3. Calculated Magnetic Susceptibilities (χ_{Tot}), Anisotropies (χ_{anis}, ppm, cgs), Magnetic Susceptibility Exaltations (λ, ppm, cgs), and Nucleus-Independent Chemical Shifts (NICS, ppm) for Cations 5, 27, and 28 and the Corresponding Anions[19a]

	χ_{tot}	χ_{anis}	λ	NICS (5)	NICS (6)	NICS (tot)
5	−1.6	58.1	32.6	54.1		54.1
27	−51.5	7.0	18.4	34.5	8.6	43.1
28	−104.4	−54.7	−0.6	24.7	1.9	28.5
5(−)	−67.7	−45.8	−17.2	−19.4		−19.4
27(−)	−124.3	−111.7	−31.9	−19.5	−12.5	−32.0
28(−)	−175.6	−174.5	−49.3	−16.4	−12.4	−41.2

VIII. Fluorenyl Cations and Analogues

A. Fluorenyl Cations

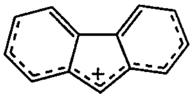
The cyclopentadienyl and indenyl cations are unambiguously antiaromatic, but the fluorenyl cation **28** is more problematic and for this reason has attracted a great deal of attention. Initial solvolytic studies of **46** indicated that fluorenyl cations **47** are difficult to form (eq 21),[25a] and the ^{1}H NMR spectrum of a substituted fluorenyl cation suggested a diminution of aromatic ring currents in this species, while efforts to generate the parent ion **28** as a long-lived species in strong acid were unsuccessful.[25b] Reaction rate measurements indicated a rate retardation by a factor of 10^3 compared to benzhydryl systems.[26] The difficulty of forming fluorenyl carbocations is reflected by pK_R values which are 4 units less than for benzhydryl derivatives,[27a] and calculations indicate fluorenyl ions are 8–10 kcal/mol less stable.[19a,27a,b] Amyes, Richard, and Novak,[27a] however, judged these energy differences to be small and not indicative of antiaromatic destabilization. This view is somewhat surprising as in many contexts an energy difference of 5 kcal/mol is considered quite large, especially so in a comparison of the benzhydryl cation which suffers from strain in attaining coplanarity and the fluorenyl cation constrained to coplanarity.



(21)

Fluorenyl cations are, however, quite readily formed and observed in flash photolysis experiments.[28] The ease of formation of fluorenyl cations from triplet precursors and the calculated[19a] greater stability of triplet compared to singlet cyclopentadienyl cation argue[28a,b] for ground-state destabilization of the fluorenyl cation due to antiaromaticity. 9-Arylfluorenyl cations react with nucleophilic solvents with rate constants approximately 2 orders of magnitude greater than those for the corresponding monosubstituted triaryl cations.[28h] Such kinetic instability was one of the early criteria for antiaromaticity, and the parent fluorenyl cation **28** has only been directly observed, on a nanosecond time scale, in the very weakly nucleophilic hexafluoroisopropyl alcohol[28d] or in zeolites.[28i]

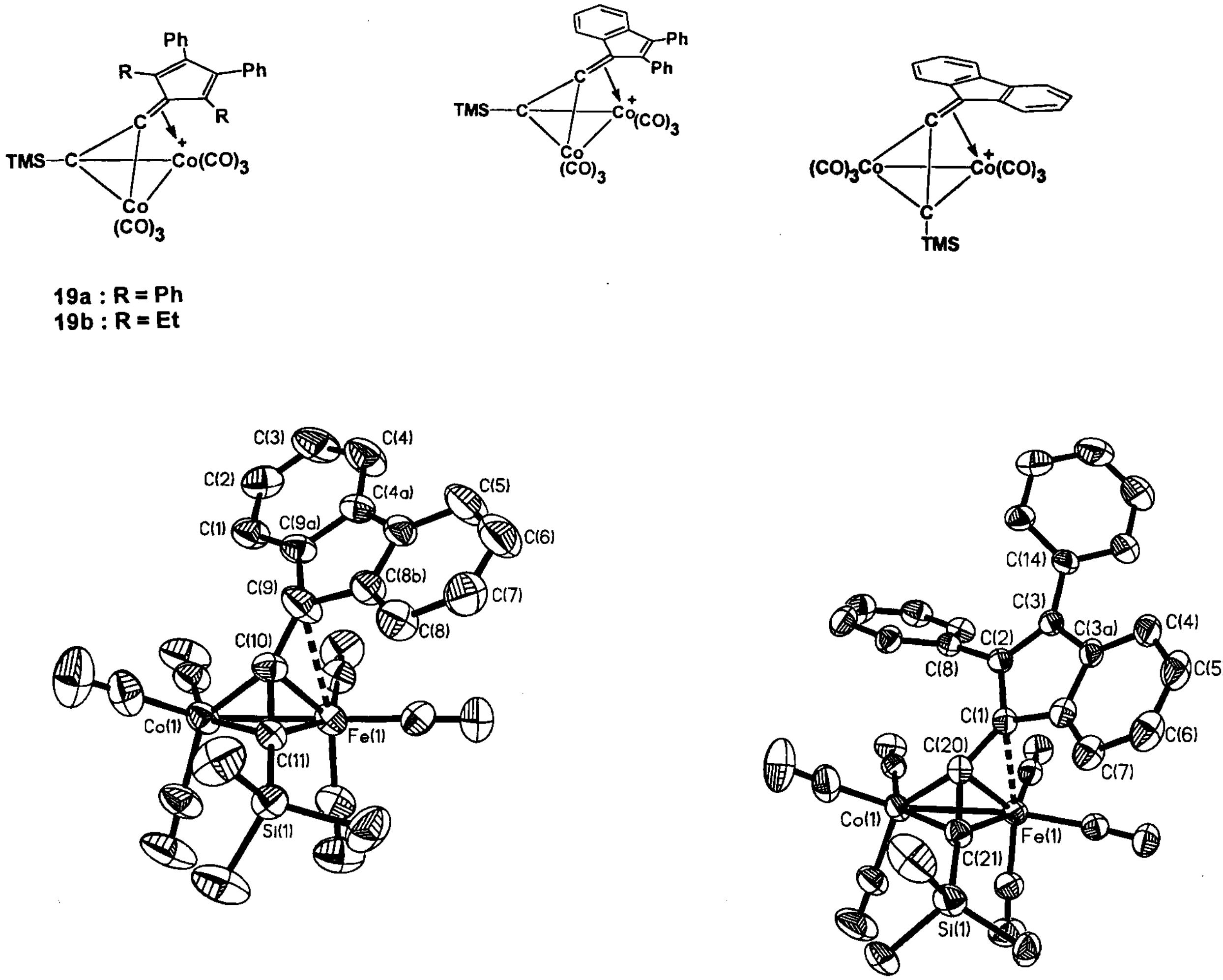
The solvolytic reactivity of the 9-CF_3 substituted fluorenyl tosylate **46** was strongly depressed compared to R = H, and a rate factor of 10^6 due to antiaromatic destabilization was estimated.[29a] Solvolytic studies with formation of 9-fluorenyl carbocations with CO_2R,[29b,c] $CONMe_2$,[29d] and $CR{=}NOCH_3$[29e] substituents have also been reported. On the basis of the calculated geometry it was suggested by Creary et al.[29d,e] that such cations avoid antiaromatic structures with cyclopentadienyl cation moieties and resemble bis(dienyl) cations **28a**.



28a

The calculated excitation energy of the longest wavelength absorption of the cyclopentadienyl cation increases upon annelation going to the indenyl and fluorenyl cations, and this is proposed as a characteristic of antiaromatic systems.[30]

Solvolytic studies of unsubstituted and 9-aryl fluorenyl derivatives **46** forming cations **47** gave depend-



19a : R = Ph
19b : R = Et

Figure 7. Structures of cyclopentadienyl, indenyl, and fluorenyl cation complexes with metal carbonyls (**48**). (Reprinted with permission from ref 32. Copyright 1999 American Chemical Society.)

ences of the rate constants on the aryl substituents and on solvent polarity that are comparable to values found for 1-arylethyl, triarylmethyl, and naphthylmethyl derivatives.[31] This behavior was interpreted as indicating that delocalization in **47** was extensive and comparable to that in these other cations and, therefore, that antiaromatic destabilization of **47** was not a significant factor. The relationship between antiaromaticity, solvation, and delocalization is complex, and potentially antiaromatic systems are proposed to reduce destabilization by delocalization, as for example in the case of the anions **17a** and **18** (vide supra) or as in **28a**.

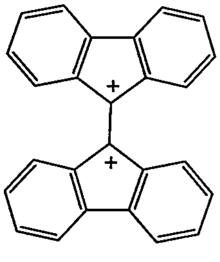
In summary, antiaromatic character of the fluorenyl carbocation is expected to be strongly attenuated. However, in a number of examples cited there is evidence for the effects of residual antiaromaticity, either in the molecule as whole or just for the cyclopentadienyl fragment.

B. Metal Carbonyl Complexed Cyclopentadienyl Cations

Cobalt tricarbonyl complexes of substituted cyclopentadienyl and indenyl cations (**48a,b**) and of fluorenyl cation (**48c**) have been studied by variable temperature NMR and X-ray structures obtained of mixed-metal $FeCo(CO)_6$ complexes of substituted indenyl and fluorenyl cations (**48d,e**) (Figure 7).[32] The results were interpreted as indicating a greater need for charge delocalization onto the metal center for the cations with the greatest antiaromatic destabilization.

C. Bisfluorenyl Dications[33]

The tetrabenzo[5.5]fulvalene dication **49** and derivatives have been generated experimentally[33a−d] and studied computationally.[33e] The ^{1}H NMR spectrum of **49** has signals at δ 5.07−5.87 with a center of gravity of δ 5.41, and the upfield shifts from the neutral precursor, with a center of gravity of δ 7.75 ppm, indicate a substantial paratropic ring current, suggesting the species is antiaromatic.[33a] The NICS values and magnetic susceptibility exaltation of **49**



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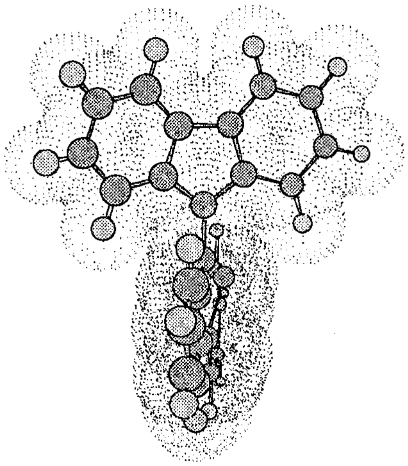


Figure 8. $\sigma-\pi$ Conjugation in the bisfluorenyl dication. (Reprinted with permission from ref 33e. Copyright 1999 American Chemical Society.)

also indicate antiaromaticity.[33e] It was suggested that for 9-substituted fluorenyl cations **47** compared to the parent fluorenyl cation **28** that the benzene aromaticity predominates and that this is increased by electron-donor groups.[33e] However, with electron-demanding substituents at C_9, there is extra electron delocalization to this position from the benzene rings, and this in turn results in enhanced antiaromaticity effects.

It is suggested that the fluorenyl rings in **49** are orthogonal, and that $\sigma-\pi$ conjugation occurs from the C−C bond of one ring to the empty p orbital of the other (Figure 8).[33a,e] This effect would explain the upfield ^{13}C shift at the carbocation center in **49**.

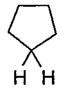
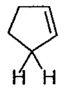
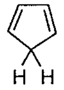
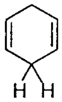
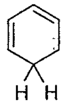
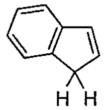
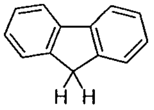
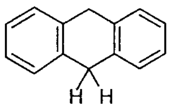
IX. Cyclopentadienyl Radical

Cyclopentadienyl radicals[34] have been known as long-lived species since Ziegler and Schnell reported the pentaphenyl derivative in 1925,[17a] and many differently substituted derivatives have been prepared. The ESR spectra of the parent cyclopentadienyl radical **6** as well as a variety of monosubstituted derivatives $RC_5H_4^{\bullet}$ (R = D, Me, Et, *i*-Pr, and *t*-Bu)[34e,f] were measured in solution. The spectrum of **6** favors a planar π-radical with average D_{5h} symmetry.[34e] This radical is expected to exist as an equilibrium mixture of five pairs of C_{2v} structures due to Jahn−Teller distortion, with a very low barrier for rearrangement. Above 70 K, all five hydrogen atoms are equivalent in the ESR spectrum, although in matrixes below this temperature the spectrum is more complex, which is ascribed to observation of the Jahn−Teller-distorted C_{2v} spectrum stabilized by the matrix.[34s]

In the monoalkylcyclopentadienyl radical, the degeneracy of the symmetric and antisymmetric molecular orbitals of the π system is broken by electron release from the substituent which destabilizes the symmetric MO, which becomes singly occupied, as indicated by the large hyperfine couping constants at H_1 and $H_{3,4}$ and the small values at $H_{2,5}$.[34e]

Estimates of the resonance stabilization energy (RSE) of cyclopentadienyl radical (**6**)[34p] and the pentamethylcyclopentadienyl radical[34h] and C−H bond dissociation energies (BDE) of precursors to **6** and higher homologues (Table 4)[35b,d,e,h] indicate these radicals are less stabilized than nonaromatic cyclic analogues. Specifically, the C−H BDE of cyclopentadiene is 5−7 kcal/mol greater than those of the cyclohexadienes and is the same as that of cyclopentene.

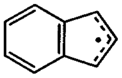
Table 4. C−H Bond Dissociation Energies (kcal/mol)[35b,d,e,h]

				
94.8	82	81.5±2.7	76.0[34v]	74.3
				
81.1±2.4	81.2±2.4	76		

Calculated nucleus-independent chemical shifts and magnetic susceptibilities for the cyclopentadienyl radical **6**[3b] are intermediate between those of the singlet cation **5** and the cyclopentadienyl anion (Table 3).[19a] The calculated ^1H chemical shift of **6** (δ 6.5) is intermediate between those calculated for singlet and triplet **5** (δ 5.2 and 8.0, respectively) and upfield from that for benzene (δ 7.8).[3b]

X. Indenyl[35] and Fluorenyl Radicals[36]

Just as for the cyclopentadienyl radical **6**, the indenyl radical **50** and the fluorenyl radical **51** are indicated by RSE and BDE (C−H) to be destabilized (Table 4). Thus, the BDE of indene and fluorene of 81.1 ± 2.4 and 81.2 ± 2.4 kcal/mol, respectively, are about 5 kcal/mol more than those of the cyclohexadienes or of dibenzocyclohexadiene forming **52**. The RSE of **51** compared to 2-propyl radical was measured as 16 kcal/mol,[36c] and the BDE of diphenylmethane (81.8 kcal/mol) was essentially the same as that of fluorene.[34m] It has been noted[35b] "radicals centered on 5-membered rings gain little additional stability by conjugation with extended aromatic networks". Considering the doubts raised about antiaromaticity in the fluorenyl cation, it is perhaps surprising there is evidence of significant destabilization in the radical **51**.



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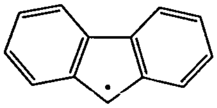

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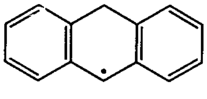

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XI. Benzene Radical Ions

A. Benzene Radical Cation[37]

The 5π-electron benzene radical cation **7** is highly reactive but was observed in 1983 by radiolysis of benzene in a $CFCl_3$ matrix at 4.2 K, and the ESR

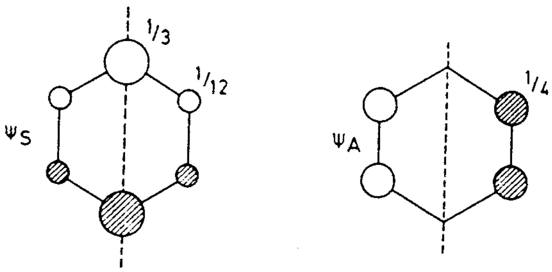


Figure 9. Benzene ψ_S and ψ_A orbitals. (Reprinted with permission from ref 37a. Copyright 1983 Royal Society of Chemistry.)

spectrum was reported[37a] as showing the unpaired electron occupied the B_{2g} orbital ψ_S of D_{2h} symmetry (Figure 9), giving a dominant hyperfine triplet. Above 100 K, the six carbons became equivalent due to dynamic averaging. More recent studies[37b,c] suggest, however, that the $^2B_{1g}$ ψ_A structure with four equivalent protons is formed in solid argon and the energies of these two states are very close, so the relative energies are determined by matrix effects.

The absorption spectrum of **7** in aqueous acidic solutions has also been detected.[37d] The vertical gas-phase ionization potential I_p of benzene was measured from the He(I) photoelectron spectrum as 9.23 eV.[37e] The standard anodic peak potential E_p could not be measured directly but was estimated from data for alkyl-substituted benzenes as 2.86 V vs NHE. Jahn–Teller distortion in **7** has been reviewed,[37f] and the high-resolution state-to-state threshold photoionization spectrum of benzene gives the shape of **7**[37g] and "diminished significantly" the "mystery" regarding the structure.[37f] The geometries, hyperfine structure, and relative stabilities of the two monodeuterated Jahn–Teller-distorted ions $C_6H_5D^{+\bullet}$ were examined theoretically and experimentally.[37h,i] EPR and ENDOR studies showed the toluene radical cation possessed the $^2B_{2g}$ structure.[37c] The IR spectra of the two Jahn–Teller forms of **7** were also calculated.[37j] On the basis of the calculated energy levels, both **7** and **8** have been classified as antiaromatic.[3c]

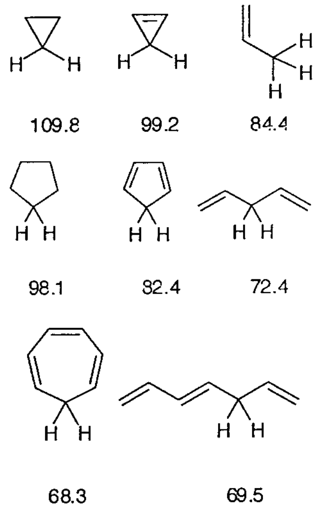
B. Benzene Radical Anion

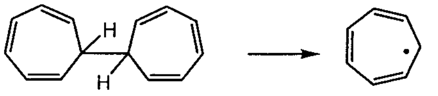
The ESR spectrum of the benzene radical anion **8**, which is the prototype of the first intermediate in the Birch reduction, was reported in 1958.[38a] This spectrum was also reported in a matrix at 121 K.[38b] Calculations of the structures of the benzene radical cation **7** and the anion **8** suggest these are quite similar with significant bond alternation: **7** C_1C_2 1.425, C_2C_3 1.358; **8** C_1C_2 1.433, C_2C_3 1.366.[38c] The radical anion of anisole was calculated to have highest electron density at the *ortho* position, and experimentally this was shown to be the preferred site for protonation.[38d]

XII. Cycloheptatrienyl Radical

The ESR spectrum of the cycloheptatrienyl radical **9** has been studied both in solution[34e,39a,b] and in matrixes,[39c,d] and the radical shows an eight-line spectrum that was assumed to arise from a planar, symmetrical structure.[39a] However, recent calculations indicate **9** is nonplanar, with C_{2v} symmetry due to Jahn–Teller distortion.[39e,f] The radical has also been studied by resonance-enhanced multiphoton ionization (REMPI)[39g] and photoelectron spectroscopy.[39h] Dissociation of bitropenyl (**53**) forming **9** as measured by ESR has $\Delta H°$ of only 35.0 kcal/mol (eq 22),[39a] indicating a weak C–C bond. This result was interpreted as indicating a high resonance stabilization of **9** of 21 kcal/mol relative to a hypothetical nonplanar form of **9**. This delocalization energy of 21 kcal/mol for **9** is less than that of 24 kcal/mol assigned to cyclohexadienyl radical **54**,[39a] which has one less conjugating double bond, and the lower stabilization of **9** may be due to the effects of antiaromaticity.

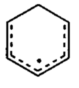
Table 5. MMEVBH Calculated C–H Bond Dissociation Energies (kcal/mol)[39i,j]





(22)

53 **9**



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Another measure of the stabilization of the cyclopropenyl, cyclopentadienyl, and cycloheptatrienyl radicals **1**, **6**, and **9**, respectively, is provided by the MMEVBH force field calculated bond dissociation energies in Table 5.[39i,j] These values indicate there is an energetic penalty for formation of **1** and **6** compared to the acyclic models, but for **9** evidence for destabilization due to cyclic conjugation is not apparent.

XIII. Cycloheptatrienyl Anion

The cycloheptatrienyl anion **10** was considered by Breslow[1] as an antiaromatic system, and previous theoretical studies by Combet-Farnoux and Berthier[40a] using Pariser–Parr calculations had found that the D_{7h} triplet was the ground state of this molecule.

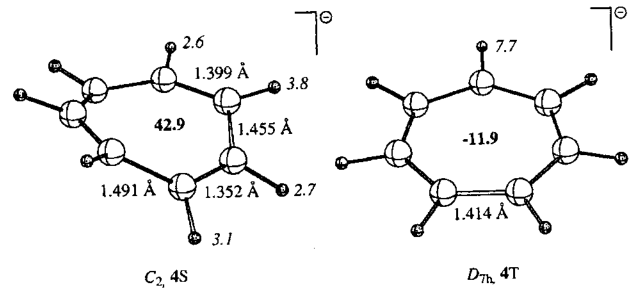
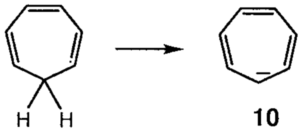


Figure 10. B3LYP/6-31G* calculated geometries of singlet (**10S**) and triplet (**10T**) cycloheptatrienyl anion. (Reprinted with permission from ref 3b. Copyright 1998 Wiley-VCH.)

Recent calculations[3b] give the singlet−triplet energy difference as −1.0 to −2.6 kcal/mol. The triplet has a planar structure with C−C bond lengths of 1.414 Å, near those of benzene (1.440 Å), while the singlet is nonplanar with an average alternation in bond lengths of 0.139 Å (Figure 10). The comparative NICS values are 42.9 for the singlet and −11.9 for the triplet, while the magnetic susceptibilities are 24.7 and −64.5, respectively, and both these criteria are strongly indicative of aromaticity for the triplet and antiaromaticity for the singlet. A low value of the excitation energy ΔE upon substituent perturbation of the energy levels is found for cycloheptatrienyl anion, and this is also used as a criterion of antiaromaticity.[30,40b] The heptaphenylcyloheptatrienyl anion was prepared by reaction of the bromide with potassium and was found to be a singlet.[40c]

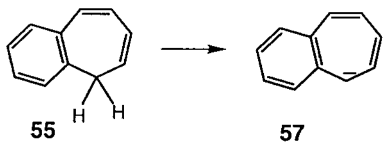
Experimental efforts to generate **10** in solution (eq 23) succeded by the reaction of cycloheptatriene with $PhCH_2K$, as well as by reaction of the MeO ether or the 7-Ph_3C derivative with Na−K alloy,[41a] and reaction of deuterated cycloheptatriene with bases.[41b,c] A pK_a value for cycloheptatriene of 36 obtained from the reduction potentials of the cation[11j] is the same as an approximate value obtained by direct equilibration.[41a] The cycloheptatrienyl anion **10** has also been generated in the gas phase by proton abstraction from cycloheptatriene,[41e,f] and the electron affinity of radical **9** forming **10** has been estimated as 13 kcal/mol.[41d,f] The anion **10** rearranges in the gas phase to the isomeric benzyl anion,[41g] which is 27.4 kcal/mol more stable.[41d,g]



10

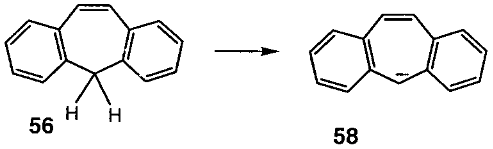
(23)

The monobenzo- and dibenzocycloheptatrienes **55** and **56** have been converted to the corresponding carbanions (eqs 24 and 25),[42,43] and ^1H NMR determinations of the anions **57** and **58** show paratropic ring currents, with upfield shifts of 3.5−4 ppm compared to cycloheptadienyl analogues.[42a] The pK_a value of **59** was 30.7, which is 1.8 units more than the open-chain analogue, and the ^1H NMR spectrum also showed a paratropic shift.[43d] The ionization of **56** is greatly enhanced upon photolysis to the excited singlet,[43a] but the high excited-state acidity of **56** is not found in **55** or in cycloheptatriene, which instead undergo photoisomerization, and this phenomenon has been examined by calculation.[42b]



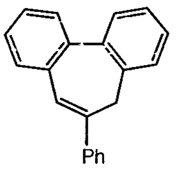
55 **57**

(24)



56 **58**

(25)



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The high acidity of **56** in the photoexcited state[43a] as well as the efficient photodecarboxylative formation of **58**[43b] are paralleled by the ease of photoionization of fluorenol forming the fluorenyl cation **28**.[28] These discoveries by Wan et al.[28a,b,43a] provide an additional useful criterion of antiaromaticity.[43c]

XIV. Summary and Outlook

Antiaromaticity has proven to be a highly useful concept and demonstrates the powerful predictive ability of the simple Hückel-derived rule. Quantitative predictions and the study of marginal cases have also provided a strong challenge both to theory and experiment. Many examples still await both vigorous theoretical examination and experimental verification, and the stimulus to achieve these goals promises to continue to advance chemical knowledge.

XV. Acknowledgments

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