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Aromaticity and antiaromaticity in fulvenes, ketocyclopolyenes, fulvenones, and diazocyclopolyenes†

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Received 2nd May 2003, Accepted 7th July 2003
First published as an Advance Article on the web 26th August 2003

The structures, energies, natural charges, and magnetic properties of 3-, 5-, 7-, and 9-membered cyclic polyenes **1**–**4**, respectively, with exocyclic methylene, keto, ketenyl, and diazo substituents (**a**–**d**, respectively) were computed at the B3LYP/6-311G+**//B3LYP/6-311+G** level to elucidate their aromatic and antiaromatic properties. The corresponding conjugated cyclic cations **1e** and **3e** were also studied. The criteria used are isomerization energies (ISE), magnetic susceptibility exaltations (Λ), aromatic stabilization energies (ASE), nucleus independent chemical shifts (NICS), and bond length alternation (Δ_R). Planar C_{2v} structures were found to be the lowest energy minima with the exceptions of diazocyclopropene (**1d**), cycloheptafulvenone (**3c**), diazocycloheptatriene (**3d**), and all of the cyclononatetraene derivatives (**4**). The fulvenes (**1a**–**4a**) have modest aromatic or antiaromatic character, and are used as standards for comparison. By these criteria the ketenylidene and diazo cyclopropenes and cycloheptatrienes **1**,**3-c**,**d** and oxo cyclopentadiene and cyclononatetraene **2**,**4b** are antiaromatic, while the 5- and 9-ring ketenyl and diazo compounds and 3- and 7-ring ketones are aromatic. The degree of aromatic/antiaromatic character decreases with ring size. The consistent agreement with Hückel rule predictions for all the criteria shows their utility for the evaluation of the elusive properties of aromaticity and antiaromaticity.

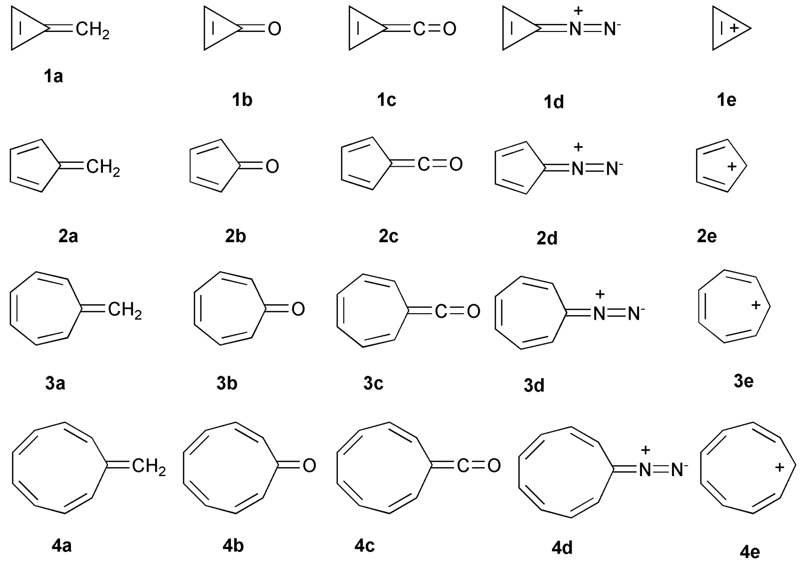
Introduction

Aromaticity is among the most widely used concepts in chemistry,[1] and the Hückel aromaticity criterion[2] accounts for the special chararacter of conjugated ring systems containing $4n + 2$ π electrons. Their extra stabilization, special reactivity, and magnetic properties are associated with the cyclic delocalization of π electrons. In contrast, conjugated planar cyclic systems with $4n$ π electrons, described as being antiaromatic by Breslow,[3] exhibit localization of the π electrons and have low stability.

Fulvenes and their analogues are cyclic polyenes with unsaturated exocyclic substituents, as represented by the triafulvene family **1** and the penta-, hepta-, and nona-analogues **2**–**4** (Scheme 1). As is summarized below, these species attract considerable attention because of their possible aromatic character. Our present investigation, extending an earlier study,[4] provides a systematic examination of a wider group of systems applying newly developed computational criteria of aromaticity, as well as a comparison with the analogous cyclic polyenyl cations.

Electronic effects in these systems may be envisaged by resonance structures in which electrons are donated to the rings or withdrawn by the exocyclic substituents (Scheme 2). For **1n**, **2o**, **3n**, and **4o** which have 4 or 8 π electrons in the ring this induces antiaromatic anti-Hückel character, and **1o**, **2n**, **3o**, and **4n**, in which there are 2, 6, or 10 π electrons in the ring, are Hückel aromatic systems.

The simplest conjugated cyclic hydrocarbon is the cyclopropenyl cation **1e**,[5] which is predicted by Hückel theory to be a relatively stable aromatic species, and this is found by experiment.[5] The analogue with an exocyclic double bond is



Scheme 1 Tria-, penta-, hepta-, and nonafulvenes (**a**), ketocyclopolyenes (**b**), fulvenones (**c**), diazocyclopolyenes (**d**), and polyenyl cations (**e**).

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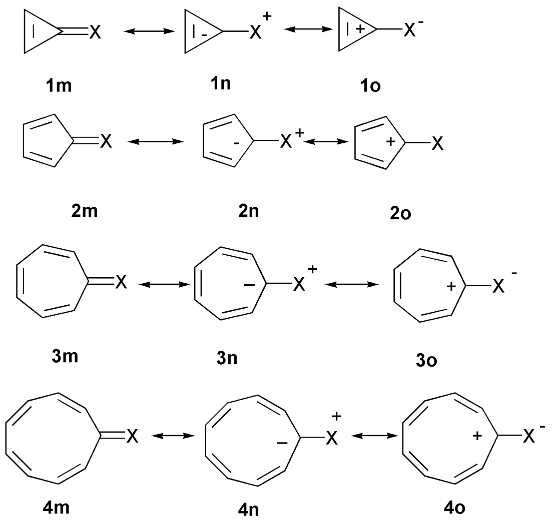
† Electronic supplementary information (ESI) available: optimized structures; bond lengths; natural charges; complete computational results (18 Tables). See http://www.rsc.org/suppdata/ob/b3/b304718k/

DOI: 10.1039/b304718k

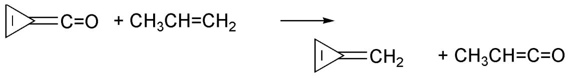


Scheme 2 Resonance structures for fulvenes.

triafulvene (**1a**), first synthesized in 1984.[6] The microwave spectrum of **1a** reveals short C–C bond lengths[7a] and a substantial dipole moment of 1.90 D, ascribed to a positively charged three-membered ring with sp^2 carbons and two π electrons, and a negatively charged exocyclic methylene, as represented by the dipolar resonance structure **1o** (Scheme 2). However theoretical calculations[7] suggest triafulvene has a relatively small resonance energy, and the contribution of the dipolar form was estimated to be about 20% of the electronic ground state.[7a] Triafulvene has differently been characterized as being aromatic,[7,8e–h] nonaromatic[7a,d,9a,b] and antiaromatic.[9d]

Cyclopropenone (**1b**), the oxo analogue of **1a**, was first reported in 1967,[10a] and many properties of this compound and its substituted derivatives have been described.[10,11] Based on its large dipole moment (μ = 4.39 D),[10d] the C=C and C=O bond lengths,[10d] high thermal stability,[12a,b] and the large charge on the oxygen of derivatives as indicated by ^{17}O NMR spectroscopy,[12d] cyclopropenone is considered to be aromatic. Calculations indicate a large resonance energy for cyclopropenone, with high negative charge on oxygen.[7d,10e,12c] The nucleus independent chemical shift as well as the magnetic susceptibility obtained by computation also indicate aromatic character for cyclopropenone.[10f,g]

Triafulvenone (**1c**), the ketene analogue of triafulvene, is not known experimentally, and experiments directed towards synthesis of a substituted derivative were unsuccessful.[13a] Computations indicated a non-planar geometry for triafulvenone,[13b] and destabilization by 17.1 kcal mol^{-1} compared to the analogue triafulvene by the comparison of eqn. (1),[4] indicating significant effects of antiaromaticity. The possible gas phase preparation of a deprotonated derivative has been reported.[13c]



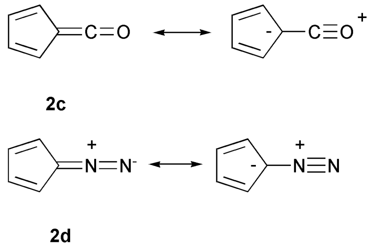
(1)

Diazocyclopropene (**1d**), which is isoelectronic to triafulvenone, is also unknown experimentally. Computational studies suggested that this species is destabilized by 22.8 kcal mol^{-1} relative to triafulvene using the method of eqn. (1).[4] The cyclopropenyl cation **1e** has been studied both experimentally and computationally, and is strongly aromatic.[5]

Substituted derivatives of pentafulvene (**2a**)[14] were first reported in 1906,[14c] and an efficient synthesis of the parent appeared in 1977.[14d] The properties of **2a** have been extensively studied, including structure determination[15] and spectral analyses.[16] The measured dipole moment of 0.424 D indicates very modest negative charge in the five-membered ring with small 6π electron character (**2n**, Scheme 2).[17] Experimental[17a] and theoretical investigations of pentafulvene concluded that it is nonaromatic.[8] Electron donor substituents on the exocyclic methylene of pentafulvene enhance conjugation and aromaticity of this species.[18]

Cyclopentadienone (**2b**) is highly reactive, but has been formed by photolysis and observed by IR and UV in an argon matrix.[19] The high reactivity of cyclopentadienone indicates significant electron withdrawal from the carbonyl carbon by the oxygen atom leading to a very unstable 4π-electron antiaromatic resonance structure **2o** (Scheme 2). The ^{1}H NMR spectrum of 1,3-di-*tert*-butylcyclopentadienone shows upfield chemical shifts for H-2 and H-4 compared to non-conjugated models,[19b] consistent with antiaromatic character.

Pentafulvenone (**2c**), the oxo analogue of pentafulvene, has been formed by photochemical Wolff rearrangement of the diazo ketone, and the kinetics of hydration to cyclopentadienyl carboxylic acid were studied.[20a] Other experimental reactivity studies[20b–d] and UV and IR spectroscopic analyses have been reported.[20b,e,f] Diazocyclopentadiene, **2d**, has been synthesized[21a] and its photoelectron, and ^{15}N and ^{13}C NMR spectra[21b] measured. Energetic comparisons analogous to that of eqn. (1) predict **2c** and **2d** to be stabilized by 4.1 and 7.8 kcal mol^{-1} relative to pentafulvene, implying aromatic stabilization.[4] The dipolar resonance structures of **2c** and **2d** show aromatic cyclopentadienyl anion character, indicating aromatic stabilization, as predicted by the *ab initio* calculations.[4]



The cyclopentadienyl cation (**2e**) is found to be highly destabilized by antiaromaticity by both experimental and computational studies,[21c] as confirmed by our recent examination.[21d]

Heptafulvene (**3a**) was synthesized more than 40 years ago[22a,b] and has been isolated and characterized by its ^{1}H-NMR, UV, and IR spectra.[22c–e] It has a modest dipole moment of 0.48 D[22f] indicating a small contribution by dipolar resonance structure **3o** (Scheme 2), with the opposite polarization compared to pentafulvene.

Tropone (**3b**) is a stable compound with a conjugated seven-membered ring system.[18a,23] The ^{1}H NMR average shifts indicate the diamagnetic ring current is enhanced in tropone[23d] as compared to heptafulvene,[22c] showing tropone has significant aromaticity due to the contribution of resonance form **3o** (Scheme 2).

Heptafulvenone (**3c**),[24] the ketene analogue of heptafulvene, was generated by the dehydrochlorination of the acyl chloride,[24a,b] and observed by IR,[24b] and was also formed by the addition of CO to the carbene from photolysis of diazocycloheptatriene.[24d] Energetic comparisons analogous to that of eqn. (1) indicate destabilization of heptafulvenone of 5.1 kcal mol^{-1} relative to heptafulvene, suggesting antiaromatic destabilization due to resonance structure **3n** (Scheme 2).[4]

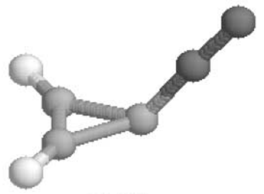
Diazocycloheptatriene (**3d**) has been generated[24d,25a–c] and calculations suggest negligible destabilization of 0.5 kcal mol^{-1} compared to heptafulvene.[4] The cycloheptatrienyl cation **3e** is a well studied and highly stabilized aromatic system.[31a]

Nonafulvene (**4a**)[26a,b] has been characterized, and there is a reference to cyclononatetraenone (**4b**)[26c] but diazocyclononatetraene (**4d**) has not been characterized, and nonafulvenone (**4c**) is unknown experimentally. The cyclononatetraenyl cation (**4e**) is antiaromatic in the Hückel configuration.[27c] The aromatic properties of these nine-membered ring conjugated systems are complicated because of their inherent flexibility (both planar and puckered arrangements are possible), and conjugation may be interrupted. In 1964, Heilbronner[27a] proposed that the presence of a Möbius-like phase inversion in the higher members of the [n] annulene series with $4n$ π electrons would lead to aromatic species. In these systems, the p orbitals are successively twisted leading to the presence of one nodal plane for the highest bonding MO. The computed Möbius twisted conformation of the positively charged 8 π electron annulene $C_9H_9^+$, the cyclononatetraenyl cation **4e**, exhibits strongly aromatic behavior.[27c] The addition of two electrons to this cation changes the molecular geometry, and leads to a 10 π-electron aromatic system.[27d,e] Large ring polyenes with a heteroatom bearing lone pairs, the heteronins, also demonstrate this effect, including the nine-membered heteroins.[27f–h]

Because of the continuing interest in the chemistry of the fulvenones and the effects of aromaticity and antiaromaticity we have extended our previous computational studies of the species. The results of calculations on triafulvene, **1a**, pentafulvene, **2a**, heptafulvene, **3a**, nonafulvene, **4a**, and their analogues where the exocyclic group X = O, C=O, and N_2 (Scheme 1) are reported, as well as results for the corresponding cations. The criteria utilized include the aromatic stabilization energy (ASE),[28] isomerization energy (ISE),[29] magnetic susceptibility exaltation (Λ),[30] nucleus independent chemical shift (NICS),[31] and bond length alternation (the difference between the longest and the shortest bond in the ring).[32]

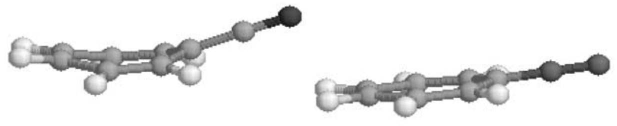
Computational methods

The geometries of the fulvene analogues **1**–**4** were optimized within chosen symmetry restrictions using the GAUSSIAN 98[33] program at the B3LYP/6-31G* and B3LYP/6-311+G** levels of density functional theory. Frequency calculations at B3LYP/6-311+G** characterized the stationary points and provided zero-point energies (ZPE).[34a] Minima were characterized by zero imaginary frequency and transition states by one imaginary frequency. The computed structures and bond lengths are shown in the electronic supplementary information (ESI Figs. 1 and 2, respectively) with natural population analysis charges (NPA, ESI Fig. 3).[34b,c] Magnetic susceptibilities were computed at CSGT-B3LYP/6-311+G**,[34d,e] using the B3LYP/6-311+G** optimized geometries. Localized molecular orbital (LMO) NICS[39] were computed (PW91/IGLO-III) at ring centers. The energies and NICS values are summarized in Table 1, and the isomerization energies (ISE), magnetic susceptibility exaltations (Λ), aromatic stabilization energies (ASE), and bond length alternations (Δ_R) are summarized in Table 2. Full computational results are given in the electronic supplementary information (Tables ESI 1–18).



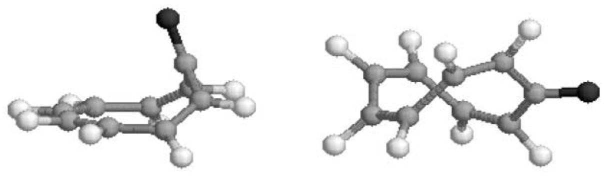
1d (C_2)

Fig. 1 Diazocyclopropene.



3c (C_2) **3d** (C_2)

Fig. 2 Heptafulvenone (**3c**) and diazocycloheptatriene (**3d**).



4b (C_S) **4b** (C_2)

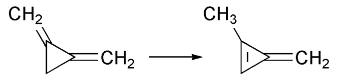
Fig. 3 Cyclononatetraenone.

Results and discussion

Triafulvene and its analogues, 1a–e

Structures with C_{2v} symmetry for triafulvene (**1a**), cyclopropenone (**1b**), and cyclopropenium cation (**1e**) are minima at B3LYP/6-311+G**. Diazocyclopropene (**1d**) with C_{2v} symmetry possesses one imaginary frequency at B3LYP/6-311+G**, and the C_s non-planar structure is a minimum on its potential energy surface (Fig. 1). For triafulvenone (**1c**) the C_{2v} planar form is favored by 0.07 to 4.91 kcal mol^{-1} relative to the C_s form at various levels of theory, while the C_s form is favored by 0.55 kcal mol^{-1} at MP4SDTQ/6-3111+G(2df,2p) (Table 2, ESI). This species is "pseudo planar", with a very flat out-of-plane bending potential energy surface. While there are variations among the various levels of theory, the highest CCSD(T) level finds the C_{2v} form to be 0.20 kcal mol^{-1} more stable than the C_s (without ZPE). The optimized structures for **1a** and **1b** agree well with experimental results.

Isomerization energies (ISE)[29] are defined as the total energy difference between a methyl derivative of the conjugated system and its non-conjugated exocyclic methylene isomer, as shown for **1f**,**g** (eqn. (2)). Since only one closely related reference compound is involved, ISE provides excellent estimates of aromatic stabilization energies (ASE) that minimize perturbing influences such as strain.



1f **1g** (2)

Magnetic susceptibility exaltation (Λ) is a measure of ring currents arising from cyclic electron delocalization.[30] Generally Λ is defined as the difference between the bulk magnetic susceptibility (χ_m) of a compound and the susceptibility (χ'_m) estimated from an increment system or from model compounds without cyclic conjugation. Aromatic compounds are characterized by negative Λ, whereas antiaromatic compounds show positive Λ. It has been suggested that magnetic susceptibility exaltation, Λ, depends not only on the square of the ring size but also on the number of delocalized electrons.[30d] The comparison of eqn. (2) employed for ISE was also applied to evaluate Λ_{ISE} values of **1a**–**e**.

As reported in Table 2 the fulvenes are chosen as reference molecules, as the contributions of dipolar resonance structures to their properties are expected to be less than for the analogous substrates. Triafulvenone (**1c**) and diazocyclopropene (**1d**) have large positive relative isomerization energies (RelISE 14.96 and 12.20 kcal mol^{-1}, respectively) as well as large relative magnetic susceptibility exaltation values (RelΛ_{ISE} 4.59 and 3.77). These effects may be attributed to antiaromaticity of triafulvenone and diazocyclopropene due to their negative charge on C_β and consequent 4π electron character in the ring (**1n** in Scheme 2).

Cyclopropenone (**1b**) is indicated to have strong aromatic stabilization arising from the 2π electron resonance structure (**1o** in Scheme 2). The RelISE (−14.72) and relative magnetic susceptibility exaltation (RelΛ_{ISE} = −3.91) values of **1b** indicate cyclopropenone is more aromatic than triafulvene, **1a**. Similarly

Table 1 Total electronic energies (au) and relative NICS values for fulvenes $(CH)_nC{=}X$

X	Symmetry	$E_{Total}{}^{a,b}$	RelNICS(0)^d	RelNICS(1)^e
CH_2 (**1a**)	C_{2v}	−154.74667	0.00	0.00
O (**1b**)	C_{2v}	−190.70030	$5.1,^c -4.0_{2\pi}, -4.2_{4\pi}$	$-2.2,^c -1.8_{2\pi}, -5.5_{4\pi}$
C=O (**1c**)	C_{2v}	−228.75521	$-3.9,^c 13.6_{2\pi}, 7.7_{4\pi}$	$4.9,^a 2.5_{2\pi}, 3.5_{4\pi}$
N_2 (**1d**)	C_s	−224.89083	$-5.6,^c 7.1_{2\pi}, 0.3_{4\pi}$	$4.2,^c 1.8_{2\pi}, -3.4_{4\pi}$
N_2 (**1d**)	C_{2v}	−224.88003	$1.8,^c 11.8_{2\pi}, 7.9_{4\pi}$	$6.8,^c 1.8_{2\pi}, 2.2_{4\pi}$
+ (**1e**)	C_{2v}	−115.76107	$-1.7,^c 0.4_{2\pi}$	$-7.3,^c -2.0_{2\pi}$
CH_2 (**2a**)	C_{2v}	−232.25518	0.00	0.00
O (**2b**)	C_{2v}	−268.18090	$9.4,^c 4.8_{4\pi}, 8.9_{6\pi}$	$6.2,^c 4.5_{4\pi}, 5.9_{6\pi}$
C=O (**2c**)	C_{2v}	−306.29587	$-9.8,^c -3.6_{4\pi}, -6.0_{6\pi}$	$-4.7,^c -3.5_{4\pi}, -4.1_{6\pi}$
N_2 (**2d**)	C_{2v}	−302.43780	$-10.3,^c -3.4_{4\pi}, -6.3_{6\pi}$	$-4.2,^c -3.1_{4\pi}, -4.0_{6\pi}$
CH_2 (**3a**)	C_{2v}	−309.68691	0.00	0.00
O (**3b**)	C_{2v}	−345.63362	$-8.7,^c -10.4_{6\pi}, -8.9_{8\pi}$	$-8.4,^c -8.4_{6\pi}, -7.3_{8\pi}$
C=O (**3c**)	C_s	−383.70751	$3.7,^c 1.3_{6\pi}, 3.9_{8\pi}$	$3.2,^c 1.0_{6\pi}, 3.6_{8\pi}$
C=O (**3c**)	C_{2v}	−383.70737	$9.0,^c 5.4_{6\pi}, 9.9_{8\pi}$	$7.9,^c 3.9_{6\pi}, 8.1_{8\pi}$
N_2 (**3d**)	C_s	−379.85197	$10.7,^c 5.8_{6\pi}, 10.4_{8\pi}$	$9.5,^c 4.0_{6\pi}, 8.3_{8\pi}$
N_2 (**3d**)	C_{2v}	−379.85197	$11.2,^c 5.1_{6\pi}, 10.8_{8\pi}$	$9.7,^c 4.2_{6\pi}, 8.6_{8\pi}$
+ (**3e**)	D_{7h}	−270.74028	$-16.5,^c -14.8_{6\pi}$	$-14.3,^c -17.7_{6\pi}$
CH_2 (**4a**)	C_2	−387.07855	0.00	0.00
CH_2 (**4a**)	C_s	−387.06435 (9.03)	0.00	0.00
CH_2 (**4a**)	C_{2v}	−387.06023 (13.00)	0.00	0.00
O (**4b**)	C_2	−423.01788	$1.0,^c 0.2_{10\pi}$	$-0.5,^c 0.4_{10\pi}$
O (**4b**)	C_s	−422.99726 (12.86)		
O (**4b**)	C_{2v}	−422.98763 (20.12)	$10.4,^c 11.2_{10\pi}$	$9.1,^c 8.6_{10\pi}$
C=O (**4c**)	C_2	−461.10986 (0.00)	$-2.5,^c -1.9_{10\pi}$	$-1.2,^c -1.4_{10\pi}$
C=O (**4c**)	C_s	−461.09584 (9.09)		
C=O (**4c**)	C_{2v}	−461.10413 (4.71)	$-7.6,^c -7.0_{10\pi}$	$-5.4,^c -6.1_{10\pi}$
N_2 (**4d**)	C_2	−457.25530 (0.0)	$-3.8,^c -3.2_{10\pi}$	$-2.3,^c -2.3_{10\pi}$
N_2 (**4d**)	C_s	−457.23847 (10.82)		
N_2 (**4d**)	C_{2v}	−457.25194 (3.06)	$-7.4,^c -6.8_{10\pi}$	$-5.2,^c -5.8_{10\pi}$

[a] B3LYP/6-311+G** (Hartrees, including ZPE). [b] Relative energies (kcal mol^{-1}) in parentheses. [c] NICS(total). [d] NICS(0) **1a** -21.7_{tot}, $-20.4_{2\pi}$, $-18.6_{4\pi}$; **2a** 0.2_{tot}, $-9.8_{4\pi}$, $-12.5_{6\pi}$; **3a** 9.6_{tot}, $-2.3_{6\pi}$, $-1.4_{8\pi}$; **4a** -0.4_{tot}, $-6.8_{10\pi}$. [e] NICS(1) **1a** -7.7_{tot}, $-2.6_{2\pi}$, $-1.8_{4\pi}$; **2a** -3.0_{tot}, $0.7_{4\pi}$, $0.0_{6\pi}$; **3a** 5.8_{tot}, $2.1_{6\pi}$, $3.1_{8\pi}$; **4a** -2.4_{tot}, $-3.3_{10\pi}$.

Table 2 Relative isomerization energies (RelISE, kcal mol^{-1}),[a–c] magnetic susceptibility exaltations (RelΛ_{ISE}),[c,d] aromatic stabilization energies (RelASE, kcal mol^{-1}),[b,e,f] and magnetic susceptibility exaltations (RelΛ_{ASE}),[b,f] and bond length alternations (Δ_R, Å), for fulvenes $(CH)_nC{=}X$

X	Symmetry	RelISE^{a-c}	Rel$\Lambda_{ISE}{}^{c,d}$	Δ_R	RelASE^{b,e,f}	Rel$\Lambda_{ASE}{}^{b,f,g}$
CH_2 (**1a**)		0.00	0.00	0.123		
O (**1b**)		−14.72	−3.91	0.087		
C=O (**1c**)		14.96	4.59	0.189		
N_2 (**1d**)		12.20	3.77	0.203		
+ (**1e**)		−43.78	−5.99	0.000		
CH_2 (**2a**)		0.00	0.00	0.122	0.00	0.00
O (**2b**)		8.83	5.64	0.172	−11.16	7.70
C=O (**2c**)		−8.44	−4.54	0.096	11.77	−6.15
N_2 (**2d**)		−9.42	−4.76	0.078	12.14	−6.88
CH_2 (**3a**)		0.00	0.00	0.095		
O (**3b**)		−5.73 (−6.21)^b	−14.68 (−17.17)^b	0.074		
C=O (**3c**)		5.55 (5.73)^b	14.77 (16.10)^b	0.114		
N_2 (**3d**)		5.57 (5.73)^b	17.99 (19.03)^b	0.114		
+ (**3e**)		−21.65 (−23.50)^b	−24.07 (−41.70)^b	0.00		
CH_2 (**4a**)	C_2	0.00	0.00	0.123	0.00	0.00
	C_{2v}			0.084	0.00	0.00
O (**4b**)	C_2	0.30	1.32	0.128	−2.86	3.89
	C_{2v}			0.103	−(9.90)^b	(31.66)^b
C=O (**4c**)	C_2	−0.40	−2.60	0.109	5.88	−7.75
	C_{2v}			0.059	(14.25^b	(−23.45)^b
N_2 (**4d**)	C_2	−0.62	−4.22	0.096	8.22	−12.88
	C_{2v}			0.053	(18.25)^b	(−24.14)^b

[a] ISE for **1a** 3.96, **2a** −1.17, **3a** −8.17 (nonplanar), **3a** −10.52 (planar), **4a** −1.55. [b] Relative planar values in parentheses. [c] From eqns. (2), (3), (5), (6). [d] Λ_{ISE} for **1a** −0.03, **2a** −2.92, **3a** 10.73 (nonplanar), **3a** 9.77 (planar), **4a** −6.42. [e] ASE for **2a** −5.66, **4a** 0.58 (planar), **4a** −0.04 (twist). [f] From eqns. (3), (6). [g] Λ_{ASE} **2a** −1.83, **4a** 4.86 (planar), **4a** −3.22 (twist).

the RelISE (−43.78) and relative magnetic susceptibility exaltation (RelΛ = −5.99) values for cyclopropenium ion (**1e**) show this has the most aromatic character in the series.

Nucleus-independent chemical shifts (NICS), introduced in 1996, provide a simple and efficient magnetic criterion of aromaticity.[31] NICS, defined as the negative absolute magnetic shielding computed at or away from the centers of rings and clusters, are now widely employed to characterize the aromaticity and antiaromaticity of two- as well as three-dimensional species and transition states.[35,36] Negative NICS values (given in ppm) indicate aromaticity (diatropic ring currents), and positive NICS values correspond to antiaromaticity (paratropic ring currents). In contrast to other aromaticity criteria, NICS does not need reference molecules or increment schemes for evaluation. While NICS correlates excellently with other aromaticity indexes based on geometric, energetic and other magnetic criteria for uncomplicated systems,[31b,37] the quantitative quality of such relationships deteriorates in more complex situations, since other effects intervene.[38a]

Several NICS refinements have been established. The first of these, "dissected NICS,"[39a] separates the total NICS at a chosen point into the component contributions, such as σ and π bonds, lone pairs, and core electrons. This "LMO-NICS" scheme, as it is now called, is based on the contributions of the localized molecular orbitals as given by the IGLO program.[39] $\mathrm{NICS}(0)_\pi$ (*i.e.*, π dissected values in the center of a ring) are recommended as NICS indexes, rather than total NICS(0). Since σ and π contributions often are in opposition, total NICS(0) can be compromised. NICS(1)[39a] values (at points 1.0 Å above ring centers where the influence of σ effects is attenuated) are recommended as alternatives to $\mathrm{NICS}(0)_\pi$ when the IGLO program is not available. Three-membered rings are a special case. Because of the importance of σ aromaticity,[39d] NICS(0) values can be quite negative (diatropic) even in the absence of π contributions. Due to the small distances involved, the $\mathrm{NICS}(0)_\pi$ values also are strongly diatropic due to the local effect of the nearby double bond. Computed NICS values were also obtained both including and excluding the contribution from the exocyclic groups; *e.g.* $\mathrm{RelNICS}(1)_{2\pi} = -1.8$ and $\mathrm{RelNICS}(1)_{4\pi} = -5.5$ for cyclopropenone (**1b**). To facilitate the interpretation and to simplify the discussion, all the RelNICS values in Table 1 are given *relative* to those of the parent fulvene. The complete NICS data are given in the Supporting Information.

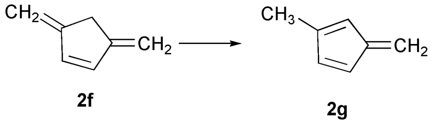
Previous computational studies of NICS and the magnetic susceptibility indicated aromatic character for cyclopropenone.[10f,g] This is confirmed by our $\mathrm{RelNICS}(1)_{2\pi}$ values (based on triafulvene, **1a**) for cyclopropenone (**1b**, −1.8) and the cyclopropenium cation (**1e**, −2.0). The $\mathrm{RelNICS}(1)_{4\pi}$ of triafulvenone (**1c**, 3.5) and of diazocyclopropene (**1d**, 2.2) show both to be antiaromatic. However for **1d** the nonplanar C_s structure (Fig. 1) is more stable by 6.8 kcal mol^{-1}, and the $\mathrm{RelNICS}(1)_{4\pi}$ shows it to be significantly less anti-aromatic than the C_{2v} form. The relative isomerization energies (RelISE) from eqn. (2) for **1b**, **1c**, **1d**, and **1e** are −14.72, 14.96, 12.20, and −43.78, respectively, indicating cyclopropenone (**1b**) and cyclopropenium ion (**1e**) are strongly aromatic, and **1c** and **1d** are strongly antiaromatic. Similarly the $\mathrm{Rel}\mathit{\Lambda}_{\mathrm{ISE}}$ values are −3.91, 4.59, 3.77, and −5.99, respectively, in agreement with the conclusions from the RelISE values.

Plots of $\mathrm{NICS}(1)_\pi$ *versus* isomerization energy (ISE), and *versus* the calculated magnetic susceptibility exaltation ($\mathit{\Lambda}$), reveal satisfactory linear correlations and demonstrate the relationship between the energy and magnetic criteria of aromaticity for the triafulvenes **1**. Table 5 (ESI) gives the coefficients for the correlation between these criteria. These trends also agree qualitatively with $\mathrm{NICS}(1)_{\mathrm{total}}$ trends (Table 1).

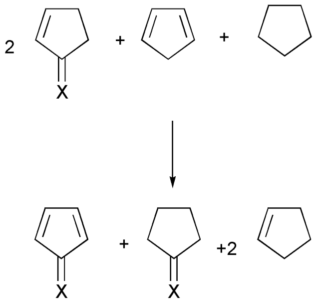
Bond length equalization is characteristic for aromatic compounds, whereas large bond length alternation (Δ_{R}) is found in antiaromatic compounds.[32] The maximum C=C *vs.* C–C difference of the three-membered ring (Δ_{R}, Table 2) is a measure of delocalization in the ring. The bond lengths are equal in the cyclopropenyl cation (**1e**), Δ_{R} = 0.0, while Δ_{R} for cyclopropenone (**1b**, 0.087), triafulvene (**1a**, 0.123), triafulvenone (**1c**, 0.189), and diazocyclopropene (**1d**, 0.203) increase, indicating decreasing aromaticity.

Pentafulvene and its analogues, 2a–d

The pentafulvenes **2a–d** have C_{2v} symmetry minimum energy structures. Relative isomerization energies (RelISE) and magnetic susceptibility exaltations ($\mathrm{Rel}\mathit{\Lambda}_{\mathrm{ISE}}$), both based on eqn. (3), for pentafulvenone **2c** (−8.44 and −4.54, respectively) and for diazocyclopentadiene **2d** (−9.42 and −4.76, respectively) indicate aromatic stabilization. In contrast, the data for cyclopentadienone **2b** (8.83 and 5.64) point to antiaromatic destabilization. The same conclusions are obtained from the aromatic stabilization energies (RelASE) and magnetic susceptibility exaltations ($\mathrm{Rel}\mathit{\Lambda}_{\mathrm{ASE}}$) of **2a–d** derived from eqn. (4) (Table 2).[38a,c]



2f **2g** (3)



(4)

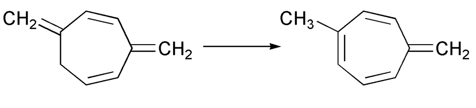
The negative $\mathrm{RelNICS}(1)_{6\pi}$ of diazocyclopentadiene and of pentafulvenone (−4.0 and −4.1, respectively), compared to pentafulvene (Table 1) are consistent with the stabilized aromatic character of the cyclopentadienyl ring. Cyclopentadienone (**2b**) is indicated to be antiaromatic by the positive $\mathrm{RelNICS}(1)_{4\pi} = 4.5$ (Table 1).

Diazocyclopentadiene (**2d**) has the smallest bond length alternation (Δ_{R} = 0.078) followed by pentafulvenone (**2c**, 0.096), pentafulvene (**2a**, 0.122), and cyclopentadienone (**2b**, 0.172). Thus, all the aromaticity criteria indicate substantial aromatic stabilization of **2c** and **2d**, but antiaromaticity in **2b**. These criteria also have been applied to the study of hyperconjugative aromaticity and anti-aromaticity in cyclopentadiene and its 5,5-disubstituted derivatives.[31b] The cyclopentadienyl cation **2e** was previously shown to be strongly antiaromatic.[21d]

Heptafulvene and its derivatives, 3a–e

Table 1 summarizes the computed total energies for heptafulvene and its derivatives (the optimized structures are shown in Fig. 1 of the ESI). Heptafulvene and tropone favor C_{2v} geometries, whereas diazocycloheptatriene and heptafulvenone have C_s energy minima (Fig. 2) and C_{2v} transition states. However, the energy differences between the various conformations are very small, *e.g.*, 0.09 kcal mol^{-1} between the C_{2v} and C_s forms for **3c**. As shown in Fig. 2, heptafulvenone bends out-of-plane more readily than does diazocycloheptatriene (**3d**). The cycloheptatrienyl cation (**3e**) favors the planar D_{7h} structure.[31a]

The isomerization energies (ISE) and magnetic susceptibility exaltations $\mathit{\Lambda}_{\mathrm{ISE}}$ for heptafulvene and its derivatives with non-planar geometries are evaluated using eqn. (5) (Table 2).[40] The $\mathrm{RelISE}_{\text{non-planar}}$ values, 5.55 for **3c** and 5.57 kcal mol^{-1} for **3d**, indicate antiaromatic destabilization. Conversely, RelISE of −5.73 for tropone **3b** and −21.65 kcal mol^{-1} for the cycloheptatrienyl cation, **3e**, characterize their aromatic stabilization. The $\mathrm{Rel}\mathit{\Lambda}_{\text{non-planar}}$ values for **3c** (14.77) and **3d** (17.99) on the one hand, and **3b** (−14.68) and **3e** (−24.07) on the other, are consistent.



3f **3g** (5)

Isomerization energies (ISE) and magnetic susceptibility exaltations (RelΛ_{planar}) (eqn. (5)) for planar heptafulvene and its derivatives (these correspond to the C_{2v} minima for **3a**, **3b**, and **3e**) show similar trends to those for the nonplanar structures (Table 2).

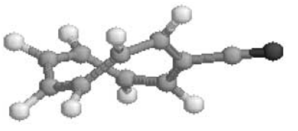
For diazocycloheptatriene **3d** the RelNICS(1)$_{8\pi}$ values (8.6 for C_{2v} and 8.3 for C_s) are larger than RelNICS(1)$_{6\pi}$ values (4.2 for C_{2v} and 4.0 for C_s), while for heptafulvenone **3c**, although there is considerable variation, the values for RelNICS(1)$_{8\pi}$ (8.1 for C_{2v} and 3.6 for C_s) and RelNICS(1)$_{6\pi}$ (3.9 for C_{2v} and 1.0 for C_s) show antiaromatic character.

For tropone (**3b**) and the tropylium ion (**3e**), the RelNICS(1)$_{6\pi}$, −8.4 and −17.7, respectively, show strong aromatic character. The trends among RelNICS(1)$_{\text{total}}$, isomerization energies (RelISE), and magnetic susceptibility exaltations (RelΛ_{ISE}) correlate well with each other (Table 5, ESI).

Bond length alternations (Δ_R) in Table 2 are based on the largest C=C *vs.* C–C bond length differences in the trienyl moieties of the seven-membered rings (*i.e.*, the ring C–C bonds to the C=X unit are not considered). The Δ_R values of 0.000 for cycloheptatrienyl cation (**3e**), 0.074 for tropone (**3b**), 0.095 for heptafulvene (**3a**), and 0.114 for both **3c** and **3d**, quantify the transition from aromaticity to antiaromaticity.

Nonafulvene and its analogues, 4a–d

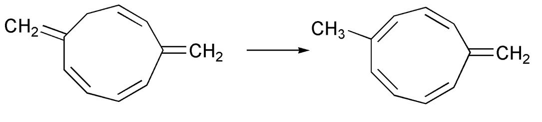
The calculated structures of **4a–d** are shown in Fig. 1 of the electronic supplementary information, and in each case the C_2 conformation is lowest in energy (Table 1). For nonafulvene (**4a**) the C_s and C_{2v} forms are transition states 9.03 and 13.00 kcal mol^{-1} higher in energy than the C_2 form, respectively, while cyclononatetraenone (**4b**) has a higher order stationary point with C_{2v} symmetry. Relaxation to lower symmetries results in a C_2 minimum of lower energy than the C_s and C_{2v} structures (Fig. 3). For nonafulvenone (**4c**) and diazocyclononatetraene (**4d**) the C_s structures are local minima 9.09 and 10.82 kcal mol^{-1}, respectively, higher in energy than C_2 (Fig. 4), showing that the 10 π electron aromatic character of these species (**4n**, Scheme 2) does not overcome the steric strain inhibiting planarity.



4c (C_2)

Fig. 4 Nonafulvenone.

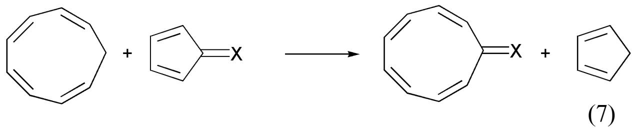
Relative isomerization energies (RelISE$_{\text{non-planar}}$) from eqn. (6) for the nonafulvenes **4b–d** are small (0.30, −0.40, and −0.62 kcal mol^{-1}, respectively), showing that aromaticity/antiaromaticity effects are not substantial in the nonplanar energy minimum structures.



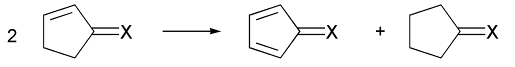
(6)

4f **4g**

Aromatic stabilization energies (ASE) and magnetic susceptibility exaltations ($\Lambda_{\text{ASE-twist}}$ and $\Lambda_{\text{ASE-planar}}$) of the twist C_2 and planar C_{2v} structures of **4a–d** and cyclononatetraene were obtained by comparison to the corresponding five-membered rings from the sum of the energies of the transformations in eqns. (7) and (8) (Table 2). This method[27h,38b] adjusts for the effect of the five-membered ring on the ASE, Λ_{twist}, and Λ_{planar}.



(7)



(8)

The RelASE$_{\text{planar}}$ values (Table 2)[38c] are −9.90 for cyclononatetraenone **4b**, indicating antiaromatic destabilization, and 14.25 and 18.25 kcal mol^{-1} for nonafulvenone (**4c**) and diazononatetraene (**4d**), respectively, indicating aromatic stabilization. Respective values of Rel$\Lambda_{\text{ASE-planar}}$ of 31.66, −23.45 and −24.14 give the same trend.

The RelASE$_{\text{twist}}$ and $\Lambda_{\text{ASE-twist}}$ differences for the more stable twist structures of **4a–d** (Table 2) are greatly attenuated compared to the less stable planar structures. Cyclononatetraenone, **4b** has RelASE$_{\text{twist}}$ of −2.86 kcal mol^{-1}, and RelΛ_{twist} 3.89, which are greatly attenuated relative to planar **4b**,[27h] but still indicative of some antiaromatic character. The RelASE$_{\text{twist}}$ values of twist nonafulvenone (**4c**) and diazocyclononatetraene (**4d**) are 5.88 and 8.22, respectively; and the Rel$\Lambda_{\text{ASE-twist}}$ values are −12.88 and −7.75, respectively. Thus both these criteria indicate that twist **4c** and **4d** display residual aromaticity, but considerably less than that for the planar structures. The ASE values indicate a similar greater stabilization of 4–5 kcal mol^{-1} for diazocyclononatetraene (**4d**) relative to nonafulvenone (**4c**).

The RelNICS(1)$_{10\pi}$ values (Table 1) for planar nonafulvenone (**4c**) and diazocyclononatetraene (**4d**) are −6.1 and −5.8, respectively, indicative of aromaticity for **4c** and **4d**, while RelNICS(1)$_{10\pi}$ of 8.6 shows cyclononatetraenone (**4b**) to be antiaromatic. For the more stable twist C_2 structures of **4c** and **4d** the relative RelNICS(1)$_{10\pi}$ are −1.4 and −2.3, respectively, indicative of weak aromaticity, while the RelNICS(1)$_{10\pi}$ value (0.4) for **4b** shows nonaromaticity. Thus, this criterion is in essential agreement with the conclusions from the ASE and Λ data.

As shown in Table 2, the bond alternations in twist nonafulvenes **4a–d** are greater than those of planar nonafulvenes **4a–d**; this is further evidence of smaller aromaticity in the twist form. The Δ_R in planar diazocyclononatetraene and nonafulvenone are small, 0.053 and 0.059, respectively. Planar cyclononatetraenone has the largest Δ_R (0.103), in agreement with antiaromatic character in **4b**.

Conclusions

The aromaticity and antiaromaticity of 3-, 5-, 7-, and 9-membered conjugated ring systems with exocyclic substituents are well characterized by energetic, magnetic, and geometric criteria. These are magnetic susceptibility exaltations Λ_{ISE} and Λ_{ASE}, isomerization energies (ISE), aromatic stabilization energies (ASE), nucleus independent chemical shifts (NICS), and the degree of bond length alternation (Δ_R). The remarkably consistent parallels between these criteria (Table 5, ESI) agree with simple Hückel considerations. The aromaticity order of cation > ketone > fulvene > diazoalkane ≈ ketene for 3- and 7-membered rings is reversed for 5- and 9-membered rings.

The quantitative aromaticity indexes describing planar and non-planar heptafulvenes **3a–e** are remarkably similar, showing that their π-electron structures are quite insensitive to geometry.

The less strained twisted C_2 structures of the nonafulvenes **4** are much more stable than the corresponding planar forms. The twisted forms display evidence for a small degree of antiaromaticity in cyclononatetraenone (**4b**), and for a similarly small degree of aromaticity in nonafulvenone (**4c**) and diazocyclononatetraene (**4d**). These effects are much larger for the planar structures.

Acknowledgements

The work in Georgia was supported by National Science Foundation Grant CHE-0209857, and that in Toronto by the

Natural Sciences and Engineering Research Council of Canada, the Petroleum Research Fund, administered by the American Chemical Society, and a Killam Fellowship from the Canada Council for the Arts.

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