Pure & Appl. Chem., Vol. 68, No. 2, pp. 209–218, 1996.
Printed in Great Britain.

What is aromaticity?

Paul von Ragué Schleyer* and Haijun Jiao
Computer-Chemie-Centrum, Institut für Organische Chemie Universität Erlangen-Nürnberg
Henkestrasse 42 D-91054-Erlangen, Germany

Definition: Compounds which exhibit significantly exalted diamagnetic susceptibility are aromatic. Cyclic electron delocalization also may result in bond length equalization, abnormal chemical shifts and magnetic anisotropies, as well as chemical and physical properties which reflect energetic stabilization. Those compounds with exalted paramagnetic susceptibility may be antiaromatic.

The history of "aromaticity", a fundamental chemical concept(1-6), began with the isolation of benzene by Michael Faraday in 1825 (7). Many definitions or criteria for characterizing aromaticity have been considered subsequently. Some milestones are:

before 1825	distinctive "aromatic" smell
before 1865	high carbon-hydrogen ratios - stable despite considerable unsaturation
1865	benzene structure (Kekulé) (8)
1866	substitution is more favorable than addition (Erlenmeyer) (9)
1910	aromatic compounds have exalted diamagnetic susceptibilities (Pascal) (10)
1925	electron sextet and heteroaromaticity (Armit-Robinson) (11)
1931	theory of cyclic (4n+2) π systems (Hückel) (12)
1936	ring current theory - free electron circulation around the benzene ring (Pauling) (13)
1937	London diamagnetism - π electron current contribution to magnetic susceptibility (14)
1956	ring currents effects on NMR chemical shifts (Pople) (15)
1969	modern study of diamagnetic susceptibility exaltation (Dauben) (16)
1970	magnetic susceptibility anisotropy (Flygare) (17)
1980	IGLO quantum chemical calculation of magnetic properties: chemical shifts, magnetic susceptibilities and magnetic susceptibility anisotropies (Kutzelnigg) (18)

These and other considerations have converged to the following criteria of aromaticity:

1. Chemical behavior—electrophilic aromatic substitution.
2. Structural—bond length equalization due to cyclic delocalization.
3. Energetic—enhanced stability (large resonance energy).
4. Magnetic—"ring current" effects.
   a) anomalous chemical shifts (15).
   b) large magnetic anisotropies (17).
   c) diamagnetic susceptibility exaltation (16).

Aromaticity is now associated with cyclic arrays of mobile electrons with favorable symmetries. In contrast, the unfavorable symmetry properties of antiaromatic systems lead to localized, rather than to delocalized

electronic structures. The "mobile electron" arrays are not restricted to π, but may be σ or mixed in character. The last is illustrated by the transition states of allowed electrocyclic reactions, which M.G. Evans described as aromatic as early as 1938 (19). Diamagnetic susceptibility exaltation is the only measurable property which is uniquely associated with aromaticity (20). We discuss below limitations in the other properties as sole criteria for characterizing aromatic compounds. None of these limitations are present with the diamagnetic susceptibility exaltations (Λ) for the same species. Generally, Λ is defined as the difference between the bulk magnetic susceptibility (χM) of a compound and the susceptibility ($\chi M'$) estimated from an increment system for the structure components (isomers without cyclic delocalization) ($\Lambda=\chi M-\chi M'$) (16). In this paper, IGLO data, which agree with available experimental estimates (18, 21), were employed.

Chemical Behavior—Electrophilic Aromatic Substitution

Not all aromatic systems react like benzene, e.g. favor electrophilic substitution over addition. Thus, many benzenoid hydrocarbons have long been known to undergo addition reactions rather than substitution (1a). Phenanthrene and anthracene add bromine and the latter serves as a diene in Diels-Alder reactions. Fullerenes are aromatic, but substitution is impossible. Addition reactions are easy for C_{60} (22); should one conclude that it is not aromatic on this basis? Clearly, the chemical reactivity criterion is not generally applicable to many kinds of systems to which the term "aromatic" has been applied.

Structural (Geometric) Criterion—Bond Length Equalization

Bond length equalization due to cyclic delocalization is the geometric criterion of aromaticity (1b, 23). In aromatic hydrocarbons, the C-C bond lengths are compared with one another and with the benzene value (ca. 1.40 Å). The direct determination of bond lengths provide valuable information on the extent of electron delocalization in molecules. In contrast, the singlet states of antiaromatic compounds are localized and generally have alternating single and double bonds which differ greatly, i.e. over 0.2 Å, in length. For example, singlet cyclobutadiene and the singlet cyclopentadienyl cation have been computed to have alternating single (1.565 Å for both) and double (1.344 and 1.355 Å, respectively) bond lengths; note that the single bond lengths are even longer than the 1.543 Å of cyclobutane at MP2(fc)/6-31G*.

However, the geometric criterion is not generally applicable. For example, borazine, isoelectronic with benzene, has six π electrons and equalized bond lengths. But the magnetic susceptibility exaltation is only -1.7 (the benzene value is -13.4); hence borazine is not aromatic. The π electrons are largely localized on the nitrogens. Singlet cyclobutadiene and cyclopentadienyl cation are highly antiaromatic; their susceptibilities are paramagnetically exalted, +18.0 and +32.6, respectively (23,24) (Tab. 1). But the C-C bond length of the antiaromatic D_{5h} triplet cyclopentadienyl cation ground state (1.425 Å) can hardly be differentiated from that of the aromatic D_{5h} cyclopentadienyl anion (1.414 Å, Becke3LYP/6-311+G**).

TABLE 1. Computed bond lengths (Å) and magnetic susceptibility exaltation, Λ (ppm cgs).

compound	benzene	borazine	cyclohexane	$C_5H_5^+$(singlet)	cyclobutadiene (singlet)
bond length	1.395	1.431	1.537	1.355; 1.565	1.344; 1.565
Λ	-13.4	-1.7	+1.1	+32.6	+18.0

In addition, bond length equalization due to π conjugation is found not only in cyclic systems but also in acyclic compounds. The allyl cation is the simplest example. The $C_5H_9N_2^+$ polymethinium cation has nearly the same C-C bond lengths at MP2(fc)/6-31G*, but is not aromatic; the calculated Λ is only -1.7

(IGLO/II//MP2(fc)/6-31G*(20). On the other hand, bond length alternation can be found in highly aromatic compounds, for example, in tetracene and phenanthrene (Fig. 1). At Becke3LYP/6-31G*, the maximum differences of bond lengths of 0.085 Å (tetracene) and 0.099 Å (phenanthrene) are scarcely smaller than the 0.102 Å range in all-trans-dodecahexaene (20). These examples show that bond length variations in the absence of other considerations can not be used to characterize aromaticity uniquely.

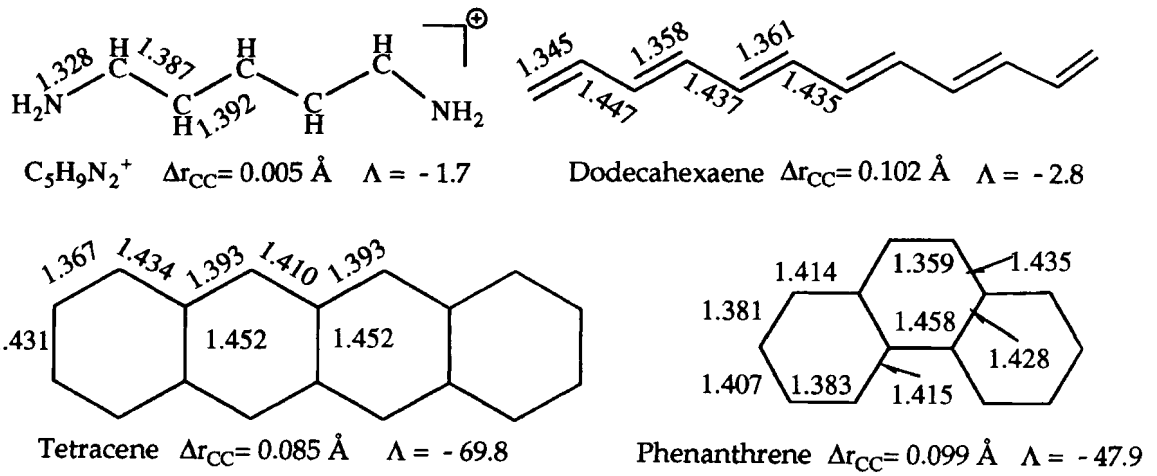


Figure 1. Becke3LYP/6-31G* optimized geometries (MP2(fc)/6-31G* for $C_5H_9N_2^+$)

Energetic Criterion—Enhanced Stability (Large Resonance Energy)

The energetic criterion of aromaticity and antiaromaticity is based on assessments of energies relative to reference systems, such as olefins or conjugated polyenes (25). For example, the hydrogenation energy of benzene is 35.2 kcal/mol lower than that of three cyclohexenes (Eq. 1, expt. data). However, estimates of this extra stability depend on the compounds taken as references, and many definitions have been suggested (25). For example, the resonance energy (RE) of benzene according to isodesmic equations are 64.2 kcal/mol (Eq. 2) and 48.9 kcal/mol (Eq. 3) (26).

3 cyclohexene = benzene + 2 cyclohexane	ΔH= - 35.2 kcal/mol	Eq. 1
3 ethylene + 3 C_2H_6 = benzene + 6 CH_4	RE= - 64.2 kcal/mol	Eq. 2
3 ethylene + cyclohexane = benzene + 3 C_2H_6	RE= - 48.9 kcal/mol	Eq. 3

Homodesmotic equations are more suitable, e.g. to evaluate aromatic stabilization energies (ASE), but these also differ. For example, ASE's for benzene are 21.7 kcal/mol via Eq. 4 (perhaps the "best" value), but 35.2 kcal/mol via Eq. 5 (26).

3 trans-butadiene = benzene - 3 ethylene	ASE= - 21.7 kcal/mol	Eq. 4
3 1,3-cyclohexadiene + cyclohexane = benzene + 3 cyclohexene	ASE= - 35.2 kcal/mol	Eq. 5

Furthermore, although cyclic delocalization of (4n +2) π electrons provides an important contribution to the overall stability of a conjugated cyclic polyene, strain effects and other contributing factors are often difficult to disentangle. These effects may counterbalance or override the influence of aromaticity (20). Thus, it is quite difficult to apply the energy criterion to strained systems; examples are C_{60}, Vogel's bridged [10]annulene, and the paracyclophanes(16c, 27). All are highly aromatic compounds with large magnetic

susceptibility exaltations (Fig. 2); the "strain" in these molecules has little effect on the ring current effects.

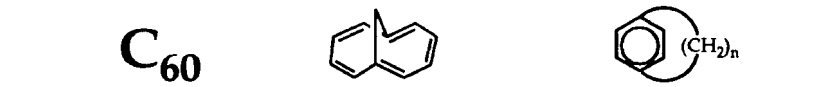


Figure 2. Diamagnetic susceptibility exaltations in strained aromatic compounds

In contrast, antiaromatic cyclobutadiene has a large destabilization energy (antiaromatic destabilization energy, ADE) of 36.3 kcal/mol (Eq 6), and exhibits a strong paramagnetic exaltation (+18.0, Tab. 1).

2 cyclobutene - cyclobutane = cyclobutadiene ADE= 36.3 kcal/mol Eq. 6

Moreover, there are highly stabilized systems, e.g. CF_4 due to anomeric effects, which can not be considered to be aromatic. At Becke3LYP/6-311++G*, the calculated homodesmotic stabilization energy of CF_4, 38.6 kcal/mol (Eq. 7), is comparable to that of benzene (Eq. 1).

$4\ CH_3F = 3\ CH_4 + CF_4$ ΔH= - 38.6 kcal/mol Eq. 7

Hence, deriations of energies of stabilization or destabilization from reference estimates (e.g. based on group enthalpy increments (26b)) are not uniquely associated with aromaticity or antiaromaticity.

Magnetic Criteria

a) ^{1}H-NMR Chemical Shifts

^{1}H chemical shifts are perhaps the most often used criteria for characterizing aromaticity and antiaromaticity. Pople suggested that the ca. 2 ppm greater deshielding of the benzene protons (7.26) relative to those of ethylene (5.28) may be a manifestation of the molecular ring current induced by an external magnetic field (15). The effects inside rings are much larger than those on the outside. In the aromatic [18]annulene, the measured ^{1}H-NMR chemical shifts of 9.28 ppm (outer protons) and -2.99 ppm (inner protons) (28) are in sharp contrast to the values for the antiaromatic [18]annulene dianion [-1.13 ppm (outer), 28.1 ppm (inner) and 29.5 ppm (inner)] (29). The difference between aromaticity and antiaromaticity is dramatic. However, this criterion is not general, since some aromatics like C_{60} and the oxocarbons (30) do not have hydrogens and ^{13}C chemical shifts in aromatic hydrocarbons are not deshielded. Also, quite large upfield fields have been found in the hydrogen bridged carbon cations (31) (Fig. 3). As a simple model system, the calculated ^{1}H chemical shift for the bridged ethyl cation is shifted upfield to -14 ppm (32). Acidic protons are deshielded. Hence, abnormal chemical shifts are not uniquely associated with aromaticity.

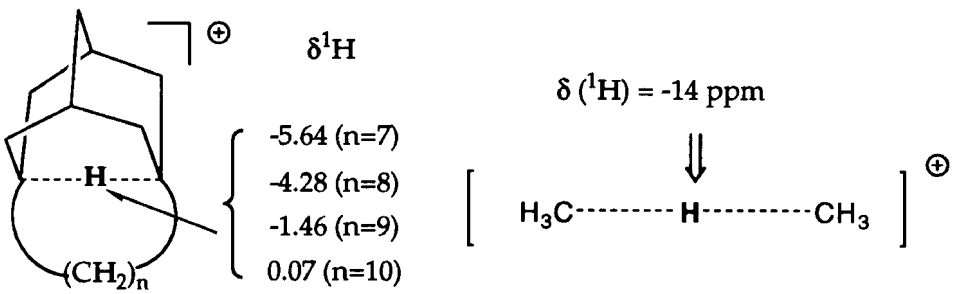


Figure 3. Abnormal ^{1}H NMR chemical shifts in non-aromatic systems.

b) Li^+-NMR Chemical Shifts

Li^+ chemical shifts and those of the isoelectronic ^3He atom are being employed as useful ring current probes (e.g. Tab. 2) (33-36). Lithium cations typically complex to the π faces of aromatic systems and the Li^+ resonance is shifted upfield due to ring current effects. For example, the Li^+ upfield shift is computed to be -6.9 in cyclopentadienyl lithium (the experimental value is δLi=-8.6, measured in THF at 25°C) and -10.8 in the sandwiched biscyclopentadienyllithium (δLi=-13.1, measured in THF at -107°C) (35). In the benzene-Li^+ complex, the calculated δLi is shifted upfield to -6.6 (24). We have used this criterion to demonstrate the aromaticity of a set of concerted pericyclic transition structures complexed with Li^+ (33). In antiaromatic compounds, however, the Li^+ resonance is downfield shifted due to paramagnetic ring current effects, e.g. 10.7 ppm in the benzene dianion dilithium complex measured by Sakurai *et al.* (36). The calculated Li^+ chemical shift is +9.2 ppm in the cyclobutadiene-Li^+ complex ($C_4H_4Li^+$) (24).

TABLE 2. Computed (measured) ^7Li chemical shifts (ppm) in aromatic and antiaromatic Li^+ complexes.

Complex	CpLi	Cp_2Li^-	$C_6H_6Li^+$	$C_6H_2(SiMe_3)_4Li_2$	$C_4H_4Li^+$
δLi	-6.9 (-8.6)[a]	-10.8 (-13.1)[a]	-6.6[b]	(+10.7)[c]	+9.2[b]

a) Ref. (35). b) Ref. (24). c) Ref. (36).

c) Large Magnetic Anisotropies

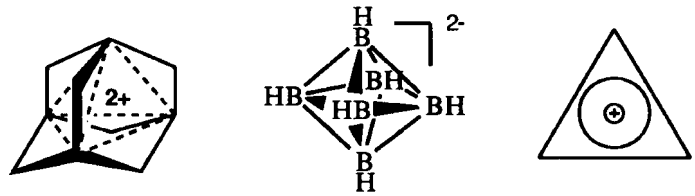
In addition to the hydrogen and lithium chemical shifts, magnetic susceptibility anisotropy has been advocated as another criterion of aromaticity (17,37). The tensor normal to the aromatic ring is much larger than the average of other tensors. Aromatic compounds have quite large negative χ_{anis}'s (Table 3). The χ_{anis} difference between benzene (-62.9) and the sum of three ethylenes (-23.1) is -39.8 ppm cgs or -36.2 relative to the trans-hexatriene value (-26.2). In contrast, highly antiaromatic compounds, such as cyclobutadiene and heptalene, have positive χ_{anis}'s (38). The anisotropy difference between cyclobutadiene and two ethylene is +44.4 ppm cgs. Table 3 compares this evidence for aromaticity and antiaromaticity with the magnetic susceptibility exaltations (the Λ's for aromatics are quite negative (diamagnetic) and significantly positive (paramagnetic) for antiaromatics).

TABLE 3. IGLO/II//MP2/6-31G* calculated magnetic susceptibility anisotropies (χ_{anis}, ppm cgs) (20).

Aromatics	χ_{anis}	Λ_{tot}	Antiaromatic	χ_{anis}	Λ_{tot}
benzene	-62.9	-13.4	cyclobutadiene	+28.7	+18.0
$C_5H_5^-$ (D_{5h})	-67.7	-17.2	$C_5H_5^+$(C_{2v}, singlet))	+58.1	+32.6
naphthalene[a]	-130.3	-28.2	cyclooctatetraene (D_{4h})	+146.3	+60.4
pyrrole	-41.8	-12.1	pentalene[a]	+12.8	+30.9
azulene[a]	-144.0	-42.9	heptalene[a]	+168.3	+76.7

a) Calculated at IGLO/DZ//Becke3LYP/6-31G*

However, χ_{anis} is only applicable for planar or nearly planar aromatic molecules and is useless for spherical systems, where χ_{anis} vanishes. Examples are the T_d symmetric 1,3-dehydro-5,7-adamantandiyl dication (**1**) and the O_h symmetric $B_6H_6^{2-}$ (**2**) (39), both are highly aromatic compounds with large diamagnetic susceptibility exaltations of -51.1 and -49.6 (Fig. 4). Note that dication has only two spherically delocalized electrons, but its exaltation is much larger than that of the cyclopropenyl cation (**3**) (-5.0).



	1, T_d	2, O_h	3, D_{3h}
χ_{anis}	0.0	0.0	- 30.5
Λ	- 51.1	- 49.6	- 5.0

Figure. 4. Comparison of magnetic susceptibility exaltations (Λ) and anisotropies (χ_{anis}, ppm cgs)

In addition, the exaltation ($\Delta\chi_{ZZ}$) of the out-of-plane magnetic susceptibly component has been considered as a criterion of aromaticity. This is defined as the difference between the measured out-of-plane component (χ_{ZZ}) and the increment value. For example, thiophene and furan have significant magnetic susceptibility exaltations (-10.0 and -9.1) and exhibit large $\Delta\chi_{ZZ}$ values of -43.4 and -24.6. However, cyclopentadiene and fulvene have quite small magnetic susceptibility exaltations (-2.4 and -3.3) and are considered to be non-aromatic compounds, but have rather large $\Delta\chi_{ZZ}$ values of -18.7 and -11.2 (Tab. 4) (37).

TABLE 4. Magnetic properties ($\Delta\chi_{ZZ}$) and (Λ, ppm cgs)

	Thiophene	Furan	cyclopentadiene	fulvene
$(\Delta\chi_{ZZ})^a$	-43.6	-24.6	-18.7 (-17.0)[c]	-11.2 (-15.9)[c]
Λ^b	-10.0	-9.1	-2.4	-3.3

a) Expt. Ref. (17f). b) Ref. (38). c) Ref. (37).

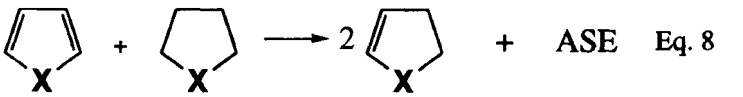
The Relationship Among Geometric, Energetic And Magnetic Criteria Of Aromaticity

Three criteria are most widely used as quantitative measures of the degree of aromaticity. To what extent are these related? Can the phenomenon of aromaticity can be described by a single index? In 1978, R.C. Haddon (40) proposed that there is an analytic relationship between the ring currents (RCs) and the resonance energies (REs) of the (4n + 2) electron annulene, where S is the area enclosed by the ring.

$$RE = \pi^2 RC/3S \qquad \text{or} \qquad RC = 3S\,RE/\pi^2$$

However, Katritzky's (41) "principle component analysis" of data sets for five- and six-membered heterocycles led to the negative conclusion that "the classical (geometric and energetic) and magnetic concepts of aromaticity are almost completely orthogonal" and that "there are at least two types of aromaticity". (The geometric and energetic criteria correlate well). Although Katritzky's analysis was based on a large number of common aromatic systems, the range of the magnetic properties was too limited in view of the likely experimental uncertainties, for a definitive assessment. Based on SINDO1 calculations, Jug *et al.* (42) found that "aromaticity is at least a two-dimensional phenomenon". The conclusions that the geometric and energetic criteria are orthogonal to each other, while the magnetic criteria correlate with the energy criteria were in contradiction to Katritzky's results (41). Again, the quality and the extent of the data employed were insufficient.

Our recent high level ab initio investigation on a comprehensive set of five-membered C_4H_4X ring systems including 4π electron antiaromatic (X=CH^+ (singlet), SiH^+, BH, AlH) and 6π electron aromatic compounds (X=CH_2, PH, SiH^-, O, S, NH, and CH^-) (23). As one example, Figure 5 shows the excellent relationship between Λ and ASE, computed using the homodesmotic equation (Eq. 8). This work demonstrated that "linear relationships exist among the energetic, geometric and magnetic criteria of aromaticity, and these relationships can be extended even to antiaromatic systems."



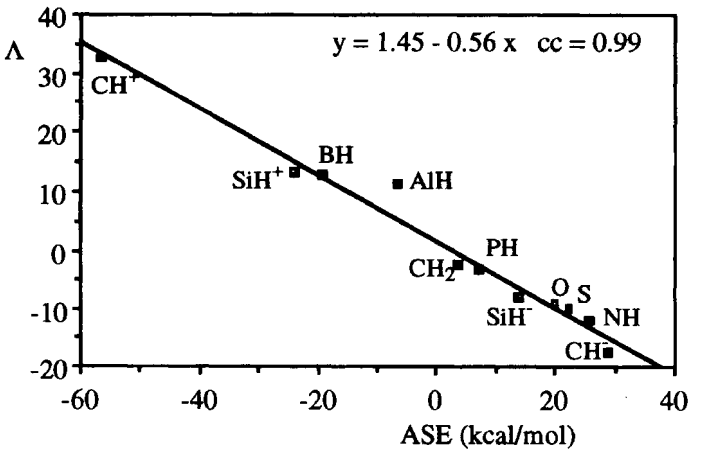
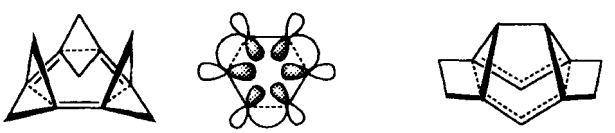


Figure 5. Correlation of the magnetic susceptibility exaltations (Λ)with ASE (Eq. 8) (23)

Aromaticity and antiaromaticity are well characterized by a combination of geometric, energetic and magnetic criteria which correlate quantitatively for such five-membered ring systems (23). Aromatic compounds are stabilized energetically and exhibit diamagnetic susceptibility exaltations and negative anisotropies as well as equalized bond lengths. In contrast, antiaromatic systems are destabilized and exhibit paramagnetic susceptibility exaltation; the single and double bond lengths are localized. However, magnetic susceptibility exaltations depend on the ring area, this must be appreciated in comparing systems of different rings.

Applications

We present some applications of the discussed criteria of aromaticity, e.g. on neutral homoaromatic systems and suggest for experimental verification (43). The first example is the "in-plane" benzene (**4**, tris(bismethano)benzene) in which the six π-orbital are in the conjugated carbon plane (in benzene they are perpendicular to the carbon plane). The other example is the bisethanosemibullvalene (**5**) (44).



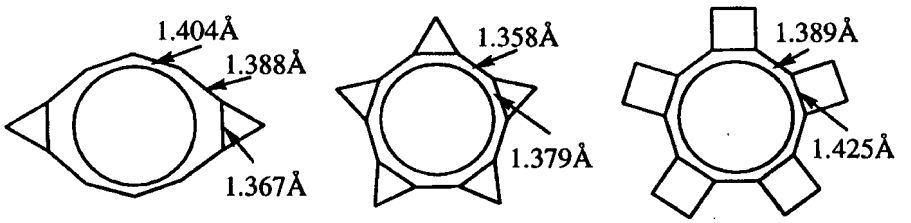
Λ = -20.9 Λ = -13.7

4, D_{3h} **5**, C_{2v}

Figure 6. Computed magnetic susceptibility exaltations for **4** and **5**

At Becke3LYP/6-31G*, both **4** (D_{3h}) and **5** (C_{2v}) are energy minima. The double bond lengths in **4** of 1.378Å are longer than the normal value and the through-space distances are 1.855 Å. Hence, **4** is delocalized geometrically. The aromaticity is evidenced by the calculated magnetic susceptibility exaltation of -41.9 based on individual increments and -20.9 by deleting the bicyclobutane unit contributions (cyclopropane rings are abnormal). Thus, **4** is quite aromatic (Λ=-13.4 for benzene). In delocalized bisethanosemibullvalene (**5**, C_{2v}), the allylic C-C bonds have the same lengths as benzene (1.396 Å) at the same level. The 1,3-through-space separations are 2.049 Å (Becke3LYP/6-31G*), i.e., in the range of C-C separations in pericyclic transition structures for the forming/breaking C-C bonds (33,45). The calculated magnetic susceptibility exaltation of -13.7 of **5** establishes its pronounced homoaromatic character.

In addition to these neutral homoaromatic compounds, we characterized several promising planar all-cis-[10]annulene derivatives **6**—**8** (46) (The parent [10]annulene isomers are all non-planar (47)).



	6, D_{2h}	**7, D_{5h}**	**8, D_{5h}**
Λ	- 64.4	- 38.1	- 61.5
ASE	- 13.9	- 18.5	- 23.0
χ_{anis}	- 207.2	- 199.4	-161.8

Figure 7. Computed bond lengths, magnetic properties (Λ, χ_{anis}, ppm cgs) and aromatic stabilization energies (ASE, kcal/mol) for planar [10]annulene systems, **6** - **8**.

At Becke3LYP/DZd, **6** (D_{2h}), **7** (D_{5h}) and **8** (D_{5h}) are energy minima. As shown in Figure 7, not only the theoretical structures (delocalized bond lengths) and energies (large aromatic stabilization energies, ASE, kcal/mol), but also the computed magnetic properties (magnetic susceptibility exaltations, Λ, and magnetic susceptibility anisotropies, χ_{anis}, in ppm cgs) demonstrate the considerable aromaticity in these "next higher" analogs of benzene. All are highly attractive candidates for experimental investigation.

Conclusion

We have discussed several of the most commonly used criteria of aromaticity. While chemical reactivity, geometric and energetic properties, and ^{1}H NMR chemical as well as magnetic susceptibility anisotropies are useful for characterizing aromaticity, magnetic susceptibility exaltation is the only uniquely applicable criterion. Our proposed definition of aromaticity is: *Compounds which exhibit significantly exalted diamagnetic susceptibility are aromatic. Cyclic electron delocalization also may result in bond length equalization, abnormal chemical shifts and magnetic anisotropies, as well as chemical and physical properties which reflect energetic stabilization. Those compounds with exalted paramagnetic susceptibility may be antiaromatic* (48).

Acknowledgment

This work was supported by the Fonds der Chemischen Industrie, the Deutsche Forschungsgemeinschaft, the Convex Computer Corporation, and the Stiftung Volkswagenwerk. We also greatly thank Prof. Dr. W. Kutzelnigg and Dr. U. Fleischer (Bochum) for helpful discussions and suggestions.

References

1. a) P.J. Garratt, *Aromaticity,* Wiley, Inc. New York, (1986). b) V.J. Minkin, M.N. Glukhovtsev, B.Y, Simkin, *Aromaticity and Antiaromaticity; Electronic and Structural Aspects*, Wiley, Inc. New York, (1994).

2. a) E.D. Bergmann, B. Pullman (Eds), *Aromaticity, Pseudo-Aromaticity, Anti-aromaticity.* Israel Academy of Science and Humanities, Jerusalem Symposium on Quantum Chemistry and Biochemistry, Vol. 3. (1971). b) R.B. Mallion, *Pure Appl. Chem.* **52**, 1541 (1980).

3. a) J.P. Labarre, F. Crasnier, *Top. Curr. Chem.* **24**, 33, (1971). b) R.C. Haddon, V.R. Haddon, L.M. Jackman, *Ibid.* **16**, Vol. 2. (1971).

4. a) D.M.G. Lloyd, *Carbocyclic Non-Benzenoid Aromatic Compounds,* Elservier, Amsterdam, (1966). b) D.M.G. Lloyd, *Nonbenzenoid Conjugated Carbocyclic Compounds*, Elservier, Amsterdam, (1984).

5. a) J.P. Snyder (Ed), *Non-benzenoid Aromatics,* Vol. 1., Academic Press, New York, (1969). b) J.P. Snyder (Ed) , *Non-benzenoid Aromatics,* Vol. 2., Academic Press, New York, (1971).

6. A.T. Balaban, M. Banciu, V. Ciorba, *Annulenes, Benzo-, Hetero-, Homo-derivatives, and their Valence Isomers,* Vol. I - III, CRC press, Inc. Boca Taton, Florida, (1987).

7. M. Faraday, *Phil. Trans. Roy. London*, 440, (1825).

8. a) A. Kekulé, *Bull. Soc. Chim.* Paris **3**, 98 (1865). b) A. Kekulé, *Ann.* **137**, 129 (1866). c) A. Kekulé, *Lehrbuch der Organische Chemie*, Vol 2. Enk. Erlangen (1866). d) A. Kekulé, *Ann.* **162**, 77 (1872).

9. E. Erlenmeyer, *Ann.* **137**, 327 and 344 (1866).

10. P. Pascal, Ann. Chim. Phys. [8] **19**, 5 (1910).

11. J.W. Armit, R. Robinson, *J. Chem. Soc.* **127**, 1604 (1925).

12. E. Hückel, *Z. Physik*, **70**, 204 and **72**, 310 (1931).

13. L. Pauling, *J. Chem. Phys.* **4**, 673 (1936).

14. F. London, *J. Phys. Radium*, **8**, 397 (1933).

15. J.A: Pople, *J. Chem. Phys.* **24**, 1111 (1956).

16. a) H. J. Dauben, Jr., J. D. Wilson, J. L. Laity, *J. Am. Chem. Soc.* **90**, 811 (1968) and **91**, 1991 (1969). b) H. J. Dauben, Jr., J. D. Wilson, J. L. Laity, "*Diamagnetic Susceptibility Exaltation as Criterion of Aromaticity*" in Non-Benzenoid Aromatics, Snyder (Ed.) Vol. 2, Academic Press, New York (1971).

17. a) R.C. Benson, W.H. Flygare, *J. Am. Chem. Soc.* **92**, 7523 (1970). b) T.G. Schmalz, C.L. Norris, W.H. Flygare, *ibid.* **95**, 7961 (1973). c) T.G. Schmalz, T.D. Gierke, P. Beak, W.H. Flygare, *Tetrahedron Lett.* **33**, 2885 (1974). d) M.H. Palmer, R.H. Findlay, *ibid.* **33**, 253 (1974). e) D.H. Hutter, W.H. Flygare, *Top. Curr. Chem.* **63**, 89 (1976).

18. W. Kutzelnigg, *Isr. J. Chem.* **19**, 193 (1980). b) W. Kutzelnigg, U. Fleischer, M. Schindler, *NMR, Basic Principles and Progress*, Vol. 23, p. 165, Springer Verlag, Berlin 1990.

19. M.G. Evans, M. Polanyi, *Trans. Faraday Soc.* **34**, 11 (1938); M.G. Evans, E. Warhust, **34**, 614 (1938) and M.G. Evans, **35**, 824 (1939). For high level ab initio computations, see references 33 and 45.

20. H. Jiao, Dissertation, Erlangen, (1995).

21. R.R. Gupta, Landolt-Börnstein, *Diamagnetic Susceptibility* (Ed, K.-H. Hellwege and A.M. Hellwege), Springer-Verlag Berlin, 1986.

22. A. Hirsch, *The Chemistry of Fullerenes*, Thieme Stuttgart, (1994).
23. P.v.R. Schleyer, P. Freeman, H. Jiao, B. Goldfuss, *Angew. Chem. Int. Ed. Engl.* **34**, 337 (1995).
24. H. Jiao, P.v.R. Schleyer, *Antiaromaticity: Evidence from Magnetic Criteria, in Proceedings of the First European Conference on Computational Chemistry* (Ed. C. Troyanowsky, Amer. Inst. Physics, Jericho, New York, 1995)
25. F. Bernardi, A. Bottoni, A. Venturini, *J. Mol. Struct. (Theochem)*, **163**, 173 (1988) and references therein (more than 60 theoretical investigations are cited).
26. The experimental data taken from: a) H.M. Rosenstock, K. Draxl, B.W. Steiner, J.T. Herron, J. Phys. Chem. Ref. data, Vol. 6. Suppl. 1. 1977. b) N. Cohen, S.W. Benson, Chem. Rev. **93**, 2419 (1993).
27. J. E. Rice, T.J. Lee, R.B. Remington, W.D. Allen, D.A. Clabo, Jr., H.F. Schaefer III, *J. Am. Chem. Soc.* **109**, 2902 (1987).
28. L.M. Jackmann, F. Sondheimer, Y. Amiel, D.A. Ben-Efraim, Y. Gaoni, R. Wolovsky, A.A. Bother-By, *J. Am. Chem. Soc.* **84**, 4307 (1962).
29. J.F.M. Oth, E.P. Woo, F. Sondheimer, *J. Am. Chem. Soc.* **95**, 7337 (1973).
30. R. West, In *Chemistry of Oxocarbons*, (Ed. R. West), Academic Press New York, 1980, Chapter 1.
31. T.S. Sorensen, S.M. Whitworth, *J. Am. Chem. Soc.* **112**, 8135 (1990).
32. C. Maerker, P.v.R. Schleyer, publication in preparation.
33. a) H. Jiao, P.v.R. Schleyer, *J. Chem. Soc. Faraday Trans.* **90**, 1559 (1994). b) H. Jiao, P.v.R. Schleyer, *Angew. Chem. Int. Ed. Engl.* **32**, 1760 (1993). c) R. Herges, H. Jiao, P.v.R. Schleyer, *Angew. Chem. Int. Ed. Engl.* **33**, 1376 (1994). d) H. Jiao, P.v.R. Schleyer, Angew. Chem. Int. Ed. Engl. **34**, 334 (1995). e) H. Jiao, P.v.R. Schleyer, *J. Am. Chem. Soc.* (1995), in press.
34. L.A. Paquette, W. Bauer, M.R. Sivik, M. Bühl, M. Feigel, P.v.R. Schleyer, *J. Am. Chem. Soc.* **112**, 8776 (1990).
35. M. Bühl, W. Thiele, H. Jiao, P.v.R. Schleyer, M. Saunders, F.A.L. Anet, J. Am. Chem. Soc. **116**, 6005 (1994).
36. S. Sekiguchi, K. Ebata, C. Kabuto, H. Sakurai, *J. Am. Chem. Soc.* **113**, 7081 (1991).
37. U. Fleischer, W. Kutzelnigg, P. Lazzeretti, V. Mühlenkamp, *J. Am. Chem. Soc.* **116**, 5298 (1994).
38. H. Jiao, P.v.R. Schleyer, unpublished.
39. a) M. Bremer, P.v.R. Schleyer, K. Schötz, M. Kausch, M. Schindler, Angew. Chem. Int. Ed. Engl. **26**, 761 (1978). b) H. Jiao, P.v.R. Schleyer, unpublished results on three-dimensional aromatic systems.
40. R.C. Haddon, *J. Am. Chem. Soc.* **101**, 1722 (1978).
41. A.R. Katritzky, P. Barczynski, G. Masummarra, D. Pisano, M. Szafan, *J. Am. Chem. Soc.* **111**, 7 (1989).
42. K. Jug, A.M. Köster, *J. Phys. Org. Chem.* **4**, 163 (1991).
43. H. Jiao, P.v.R. Schleyer, *ISNA-8 Abstracts*, Poster 73, Braunschweig, Germany, 1995.
44. R.V. Williams, H.A. Kurtz, *J. Org. Chem.* **53**, 3262 (1988).
45. K.N. Houk, Y. Li, D. Evanseck, *Angew. Chem. Int. Ed. Engl.* **31**, 682 (1992).
46. P.v.R. Schleyer, H. Jiao, H.M. Sulzbach, H.F. Schaefer III, *J. Am. Chem. Soc.* (1995) submitted.
47. M.H. Sulzbach, P.v.R. Schleyer, H. Jiao, Y. Xie, H.F. Schaefer III, *J. Am. Chem. Soc.* **117**, 337 (1995).
48. P.v.R. Schleyer, *ISNA-8 Abstracts*, Lecture 1, Braunschweig, Germany, 1995.