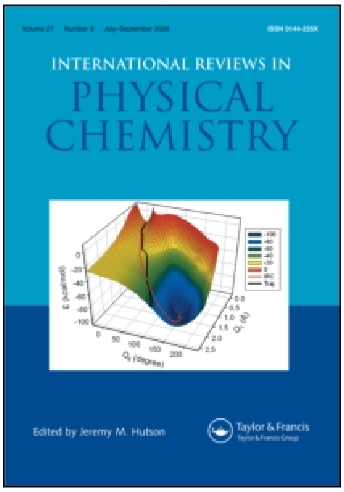

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Measuring aromaticity

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Measuring aromaticity

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Aspects of the aromaticity concept are reviewed: aromatic characters and measures of aromaticity. Aromatic character is defined by certain physical and chemical properties that characterize cyclic organic molecules, including stability, reactivity, and ring current effects. Measures of aromaticity are numerical indices devised to understand and to predict aromaticity. Emphasis is put on recent developments of theoretical indices, especially the gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) or chemical hardness.

1. Introduction

The chemistry of aromatic compounds began with the discovery of the benzene molecule in the condensate of a compressed illuminating gas by Faraday in 1825. It was Kekulé who first used the term 'aromatic compounds' as a name for describing benzene and its derivatives because of their odour. The idea of aromaticity has developed so dramatically that its original meaning has been completely lost. Though the chemistry of aromatic compounds, both theoretical and experimental, has flourished over recent decades, the most important step in the development of the concept of aromaticity already was accomplished by Kekulé, in his papers proposing the structure of benzene (Kekulé 1865a, b, 1866). Thereby was established the connection between the aromatic character of a molecule and its cyclic structure.

Continuing controversy on aromaticity has been the driving force both for syntheses of many interesting molecules and for the development of many theoretical arguments (see, for example, Bergmann and Pullman (1971)). Aromaticity is no doubt among the concepts most used by chemists, but as yet there is no precise definition of it accepted by the whole chemical community. This comes from the fact that no directly measurable physical and/or chemical properties can be attributed uniquely to aromaticity. Aromaticity has many facets including, among other things, high thermal stability, low reactivity, and sustained induced ring current. Most would accept the qualitative statement that *Aromaticity of a conjugated molecule is the set of properties associated with cyclic conjugation.* This is a fine subjective definition, but one wants more quantitative measures.

Though no experimental techniques exist to determine the contribution to a particular property from cyclic conjugation theoretical determination is possible. One successful way to relate aromaticity with cyclic structure is to use a hypothetical reference structure to eliminate all the 'acyclic' contributions of the molecule. Hence the thermal stability of an aromatic molecule can be measured either by the energy difference of the molecule and its reference structure (see, for example, Dewar and de Llano (1969)) or their hardness difference (Zhou and Parr 1989). An extra stability so obtained is, by definition, the aromaticity. Theoretical indices devised to measure this extra stability and other cyclic-conjugation-related properties will be discussed in detail in the following sections.

In this article we review, without pretending to be comprehensive, the theories of aromaticity that have been used by chemists. We first describe some of the properties of an aromatic compound—the aromatic character. We then discuss and comment on the theories of aromaticity developed over the last twenty years.

A word of caution is necessary. Since aromaticity, is a set of properties, it is not surprising that exceptions exist to all measures we are going to survey here.

For historical development and synthetic aspects of the aromaticity concept, the reader is referred to other reviews (Ginsburg, 1959, Sondheimer 1966, Jones 1968, Badger 1969, Garratt and Sargent 1969, Baird 1971, Bergmann and Pullman 1971, Dewar 1971, Agrant 1973, Breslow 1973, Cook *et al.* 1974, Lewis and Peters 1975, Perlstein 1977, Garratt 1986, Lloyd 1989, Gorelik 1990).

2. Aromatic character

Aromaticity is not a single but a multi-faceted property. All specific properties resulting from cyclic conjugation are evidence for aromaticity. In this section we describe the most important aromatic characteristics.

2.1. *Thermal stability*

More precisely, this should be called extra thermal stability since we are really talking about that portion of the stability resulting from any cyclic conjugation that may be present. The energy corresponding to this extra stability is conventionally called resonance energy (*RE*).

Numerical values of *RE* can be obtained both empirically and theoretically at various levels of sophistication. The *RE* for a molecule is the quantity obtained by subtracting the actual energy of the molecule from the energy of the most stable contributing resonance structure. The empirical determination of *RE* usually employs heat of formation, heat of hydrogenation, or heat of combustion (see, for example, Wheland (1955)). Heat of atomization, along with bond energies assumed constant from molecule to molecule (see, for example, Coulson (1961)), also gives *RE*. Heats of atomization and bond energies can be determined theoretically and experimentally.

There is another quantity closely related to *RE*, the bond separation energy (see, for example, Hehre *et al.* (1986)). Bond separation energy has been used as an alternative of *RE* for describing aromaticity (Krogh-Jespersen *et al.* 1981, Gordon *et al.* 1983, Bock *et al.* 1984, Cremer *et al.* 1985, Nagase *et al.* 1985, Budzelaar and Schleyer 1986, Hehre *et al.* 1986, Sax and Janoschek 1986, Kuwajima and Soos 1987, Slatey *et al.* 1987, Boldridge and Gordon 1988 *a*, *b*). Bond separation energy is defined as the energy of a reaction which separates all formal bonds between heavy atoms (non-hydrogen bonds) into the simpler parent (two-heavy-atom, four-heavy-atom, or six-heavy-atom) molecules containing these same kinds of linkages. Typical bond separation reactions are isodesmic (with two-heavy-atom products), homodesmic (with four-heavy-atom products), or hyperdesmic (with six-heavy-atom products) reactions (Nagase *et al.* 1985, Hehre *et al.* 1986). The values from different reactions are different. When comparisons are being made, the same type of reaction should be used.

The difference between *RE* and bond separation energy, though subtle, is not necessarily small. *RE* assumes a reference structure of localized single and double bonds with somewhat fixed bond energies from molecule to molecule. For bond separation energy, the bond separation reaction of a particular type considers only bond type without assuming a bond energy. For example, the isodesmic bond separation reactions for benzene and cyclobutadiene are $C_6H_6+6CH_4 \rightarrow 3CH_3\text{–}CH_3 + 3CH_2\text{=}CH_2$ and $C_4H_4+4CH_4 \rightarrow 2CH_3\text{–}CH_3+2CH_2\text{=}CH_2$ respectively. These reactions alone give bond separation energies for these two molecules. The calculation of *RE*, on the other hand, uses fixed bond energies for C–C, C=C and C–H bonds of the classical Kekulé structure in both molecules. A problem in using bond separation energy is that there are contributions to it from polyenic delocalization.

2.2. *Kinetic stability*

Aromatic systems tend to be easily produced and to be retained in all kinds of reactions. Hence when a reagent attacks an aromatic molecule, substitution reactions prevail over addition reactions. Reactivities toward substitution, or addition, or both, have been used to measure the aromaticity of a molecule (Cassidy *et al.* 1968, Dixon 1970, Clementi *et al.* 1974, Hirsch *et al.* 1975, Doddi *et al.* 1976, Wightman *et al.* 1976, Horak *et al.* 1979, Ohmae *et al.* 1981, Nudy *et al.* 1987, Bofill *et al.* 1988). The competition between substitution and addition has been claimed to be a much better criterion of aromaticity than any other reactivity index (Dixon 1970, Bofill *et al.* 1988). The result of the competition can be observed by experimentally determining the products of the competing reactions, or by theoretically computing the relative rates. For example, for the σ-complex cations of cyclobutadiene and benzene, respectively, the activated complex theory predicts a rate constant ratio for H^+ abstraction (substitution reaction) against H_2O addition (addition reaction) of $2{\cdot}1\times10^{-24}$ and $1{\cdot}2\times10^9$, so that cyclobutadiene is antiaromatic and benzene is aromatic (Bofill *et al.* 1988). Antiaromaticity is the opposite of aromaticity.

2.3. *Induced ring current*

This is not a directly observable current, but its existence can be inferred from the diamagnetic anisotropy, diamagnetic susceptibility exaltation, or unusual chemical shifts in nuclear magnetic resonance (NMR) spectra (Pauling 1936, London 1937, Pople 1958, Waugh and Fessenden 1957, McWeeny 1958, Dauben *et al.* 1968). These properties are often employed as criteria for aromaticity, though use of the ring current effect has been criticized (Pople 1964, Ferguson and Pople 1965, Musher 1965, 1966, 1967, Abraham and Thomas 1966, Gaidis and West 1967, Blustin 1980, Lazzeretti and Zanasi 1981, 1983, Lazzeretti *et al* 1982a, b). Now practising chemists frequently use the chemical shift of NMR spectra as their criterion of aromaticity (there are hundreds of papers taking this viewpoint).

The diamagnetic anisotropy is defined as $\Delta\chi=\chi_z-\frac{1}{2}(\chi_x+\chi_y)$, where χ_x, χ_y, and χ_z are the three principal components of the diamagnetic susceptibility. The diamagnetic anisotropy as an aromatic measure derives from the pioneering work of Pauling, who derived the connection between induced ring current and diamagnetic anisotropy employing a free electron model for p_z electrons (Pauling 1936). Direct measurement of anisotropy is difficult and can only be accomplished with crystalline substances. This limits its usage as an aromatic criterion. However, there are indirect ways to determine $\Delta\chi$, and so the diamagnetic anisotropy sometimes is still employed (Davies 1974, Lazzeretti and Taddei 1974, Palmer and Findlay 1974, Battaglia and Ritchie 1977, Blustin 1979, Calderbank *et al.* 1981, Ritchie 1982). Further analysis showed that it is the non-local contribution to diamagnetic anisotropy $\Delta\chi^{\text{non-local}}$ that is responsible for the correlation with electron delocalization and hence measures the aromatic character (Schmalz *et al.* 1974, Burnham *et al.* 1977).

The diamagnetic exaltation is the difference between the susceptibility exhibited by a compound and that predicted for the identical but not cyclically delocalized structural counterpart: $\Lambda=\chi_{\mathrm{M}}-\chi_{\mathrm{M}'}$, where $\chi_{\mathrm{M}}=(\chi_x+\chi_y+\chi_z)/3$. χ_{M} can be measured experimentally and $\chi_{\mathrm{M}'}$ can be calculated using empirical constants for separate structural ingredients (Craig 1959, Dauben *et al.* 1968, Ege and Vogler 1972). Take benzene as an example. The M′ now is cyclohexatriene. $\chi_{\mathrm{M}}=54{\cdot}8\times10^{-6}\,\mathrm{cm}^3\,\mathrm{mole}^{-1}$ (Smith 1960). $\chi_{\mathrm{M}'}$, according to Haberditzl (1966), is a sum of contributions from several components (use Haberditzl's terminology): $\chi_{\mathrm{M}'}=6(\mathrm{C}^*\text{–}\mathrm{H})+6(\mathrm{C}^*\text{–}\mathrm{C}^*)+6(\mathrm{C}$ inner electron cores$)+3(\mathrm{C}\pi$ bonds$)=(6\times3{\cdot}2+6\times2{\cdot}4+6\times0{\cdot}15+3\times2{\cdot}2)\times10^{-6}\,\mathrm{cm}^3\,\mathrm{mole}^{-1}=41{\cdot}1\times10^{-6}\,\mathrm{cm}^3\,\mathrm{mole}^{-1}$. Hence $\Lambda=13{\cdot}7\,\mathrm{cm}^3\,\mathrm{mole}^{-1}$. This index is good qualitatively but not quantitatively. There is an argument from perturbation theory that the magnetic susceptibility component perpendicular to the molecular plane should be a more reliable aromaticity index (Benassi *et al.* 1975).

The pronounced H^1-chemical shift of a monocyclic conjugated molecule like [n]annulene is associated with aromatic and antiaromatic ring currents as table 1 shows. It is easy to visualize how NMR chemical shift relates to induced diamagnetic ring current from a simplified picture for an aromatic ring as shown in figure 1 (see, for example, Lowry and Richardson (1987)). The induced field H', due to the induced diamagnetic ring current, has opposite directions inside and outside the ring. For resonance to occur a higher field H (upfield) has to be applied for inner protons and a lower field H (downfield) for outer protons. For $4n$ rings, the induced ring current is paramagnetic. The chemical shift will be downfield for inner protons and upfield for outer protons. However, the paramagnetic ring current will be partly quenched by alternation of bond lengths and molecular non-planarity (Pople and Untch 1966). The observed results for $4n$ rings may be due to local anisotropies that are anomalous for the crowded inner protons (Barfield *et al.* 1975). Conventionally a compound which has an ability to sustain an induced diamagnetic ring current is called diatropic and a compound is called paratropic if it sustains a paramagnetic ring current. Several theoretical studies have delineated the relationships between chemical shift and

Table 1. Relationship of H^1-chemical shift with ring current for monocyclic molecules.

	Aromatic ring current (diatropic)	Antiaromatic ring current (paratropic)
Inner H	Upfield	Downfield
Outer H	Downfield	Upfield

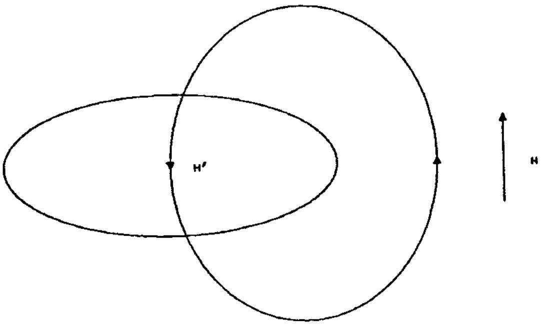

Figure 1. Rough illustration of direction of induced field H' generated by diamagnetic ring current induced by applied field H for $4n+2$ monocyclics.

induced ring current (Waugh and Fessenden 1957, McWeeny 1958, Pople 1958, Haddon 1972, Vogler 1984, Ohmae *et al.* 1985, Facelli *et al.* 1987). Again the non-local contribution to chemical shift is important (Ege and Vogler 1975).

For any quantity related to induced ring current, it is the so-called paramagnetic portion of the quantity that is related to induced ring current. Take the diamagnetic susceptibility as an example. The z component of χ_M is, according to Van Vleck (1932)

$$\chi_{M,z} = -\frac{Ne^2}{4mc^2}\sum_i \langle 0|x_i^2+y_i^2|0\rangle + \frac{Ne^2}{2m^2c^2}\sum_{n\neq 0}\frac{|\langle 0|\hat{m}_z|n\rangle|^2}{E_n-E_0}, \tag{1}$$

where N is the Avogadro constant, m and e are respectively the mass and the charge of an electron, c is the speed of light, x_i and y_i are the x and y components of the position vector of the ith electron in the molecule, $\hat{m}_z$ is the z component of the angular momentum vector, $|n\rangle$'s are the eigenstates of the molecule, E_n's are the corresponding energies, in which '0' refers to the ground state of the molecule. The first summation in (1) is taken over all electrons. The second summation runs over all eigenstates except the ground state. The contribution from the induced ring current is the second term, which is always positive (paramagnetic). When this term is relatively small (large) we say the induced ring current is diamagnetic (paramagnetic). The diamagnetic contribution (the first term) remains relatively constant (Schmalz *et al.* 1974).

2.4. *Other aspects of aromatic character*

It is electron delocalization over a cyclic conjugated system that results in aromaticity. An aromatic molecule shows little or no single and double bond alternation. The bond orders of all cyclic conjugated systems should be more or less the same. The degrees of electron delocalizations, bond lengths, and bond orders can be determined both experimentally and theoretically (Bertelli *et al.* 1969, Bailey *et al.* 1970, Yoshida *et al.* 1971, Lazzeretti and Taddei 1974, Machiguchi *et al.* 1974, Ottersen 1974, Schreiner *et al.* 1975, Gavezzotti and Simonetta 1976, Chacko *et al.* 1977, Olah and Grant 1977, Jones and White 1978, Destro *et al.* 1980, Kabuto and Oda 1980, Gerson *et al.* 1980, Loos and Leška 1980, Cordell and Boggs 1981, Destro *et al.* 1981, Harel and Manassen 1981, Hutton *et al.* 1981, Amato *et al.* 1982, Facelli *et al.* 1983, Staab *et al.* 1983, Bock *et al.* 1984, Walther *et al.* 1984, Bonnett *et al.* 1985, Friedman and Allen 1986). If heteroatoms are involved, usually there are charge transfers upon formation of an aromatic system (Farnham and Mislow 1972, Mathey 1976, Hase *et al.* 1978).

Physicochemical properties, such as acidity (or basicity), dipole moment, polarographic reduction potential, u.v. absorption, photoelectron spectrum (PE), and polarizability are sometimes employed as indicators of aromaticity (Balaban 1969, Brown and Ghosh 1969, Feldman and Flythe 1969, Breslow and Washburn 1970, Bradamante *et al.* 1971, Breslow 1971, Boschi *et al.* 1972, Agranat and Pick, 1973, Allen *et al.* 1974, Bickelhaupt and van Mourik 1974, Cook *et al.* 1974, Oth *et al.* 1974, Semmelhack *et al.* 1976, Vos *et al.* 1976, Olszowski *et al.* 1979, Bordwell *et al.* 1981, Wudl 1982, Baumann and Oth 1982, Ritchie 1983). Recent *ab initio* calculations show that the second-order polarizability decreases significantly as the aromatic character increases (Meyers *et al.* 1991). Also notable is the connection of the mean vibrational amplitudes of C–C bonds in a molecule with its aromaticity, agreeing with the correlation of bond order with mean vibrational amplitude (Gebhardt 1973, Campos-Vallette *et al.* 1988). Somewhat related are deformation energies, inversion barriers, and rotation barriers, all of which can reflect the aromaticity of a molecule (Downing *et al.* 1969, Egan *et al.* 1970, Figeys and Dralants 1971, Wife and Sondheimer 1974, Podlogar *et al.* 1988). For example, the energy needed to deform a benzene molecule is much higher than the energy needed to deform, to the same degree, a cyclobutadiene with D_{4h} symmetry of C–C bond length 1·39 Å. The aromatic molecule is more difficult to deform.

Tautomerism can be affected by aromaticity if an aromatic structure is involved. Hence tautomeric equilibria can provide the basis for a scale of aromaticity for a set of related aromatic molecules (Stacy and Wollner 1967, Cook *et al.* 1971, 1972a, b, 1973, Cook *et al.* 1974, Carmody *et al.* 1976, Cook *et al.* 1976).

2.5. *Effects on aromaticity*

For a conjugated system, maximum pπ orbital overlap demands planarity of the molecule. Deviations from planarity reduce the ability of π electrons to delocalize, hence reduce the aromaticity (or antiaromaticity) (Vogel 1971, Wife and Sondheimer 1974, Vogel *et al.* 1980, Vogel *et al.* 1981, Ogawa *et al.* 1983, Wijesekera *et al.* 1983, Ullah *et al.* 1985, Vogel *et al.* 1986, Podlogar *et al.* 1988). A closely related factor which also affects aromaticity is strain that can exist in the σ-framework. In a few cases the strain destabilization dominates to the degree that aromaticity is completely suppressed. An often quoted example in discussing relationship between strain and aromaticity is [n]cyclophane (von Zijl *et al.* 1986, Remington *et al.* 1986, Rice *et al.* 1987, Jennesken *et al.* 1987, Lee *et al.* 1988a, b). For example, [5]- and [6]paracyclophane are not aromatic by the bond separation energy criterion. The strained structure destroys the planarity of the benzene ring in the molecule, and hence destroys the aromatic character of the molecule. Other molecules have been examined also (Weiss and Andrae 1974, Schmidt *et al.* 1978, Rabinovitz and Willner 1980, Leška and Loos 1984). Strain-caused distortions are more pronounced in small rings (Santiago *et al.* 1978).

Annelation affects aromaticity, usually in a predictable way. For example, fusion of two aromatic molecules will result in a molecule less aromatic than its two parents (Jones *et al.* 1975, Mitchell and Carruthers 1975, Morigaki *et al.* 1975, Weavers *et al.* 1975, Rabinovitz *et al.* 1979, Kruszewski 1980, McCzgue *et al.* 1984, Meot-Ner *et al.* 1988). When a ring is added to a molecule (fusion) the aromaticity of the resulting polycyclic molecule generally depends on bond order of the attached bond and aromaticity of the attaching ring (Kruszewski 1980).

If a substituent is present, the delocalized electron density in an aromatic species will be affected (Tomasik and Krygowski 1974, Stibor *et al.* 1975). If the substituent is attached to a heteroatom which provides a lone pair in the aromatic system, then the substituent will affect the availability of the lone pair for delocalization into the ring (Anastassiou and Elliott 1974). The electronegativity of the heteroatom can also influence aromaticity of the heterocyclic system (Anastassiou *et al.* 1974).

When a cyclic molecule is coordinated to a metal atom (or a metal complex), its aromaticity is affected by the metal atom, through charge transfer or/and electrostatic interaction (Guimon *et al.* 1985, Lewandowski and Janowski 1988). A famous example of formation of an aromatic complex via charge transfer is ferrocene (see, for example, Parkins and Poller (1986)). Aromaticity of aromatic molecules decreases upon coordination to metals (Kalbacher and Bereman 1976, Clack and Warren 1978, Elschenbroich *et al.* 1984). But some localized rings can be stabilized through coordination to metals (Miller and Dixon 1987). Usually the stability of the complex decreases as the aromaticity of the ligand increases (Verchere 1978).

Finally, the Coulomb repulsion in small rings with two negative charges can cause loss of aromaticity (Garatt and Zahler 1978).

3. Theoretical measures of aromaticity

Hückel's $4n+2$ rule for predicting aromaticity, which says that monocyclic conjugated molecules with $4n+2$ electrons are aromatic while those with $4n$ electrons are antiaromatic, has played a leading role in the theory of aromaticity. This rule was derived from Hückel molecular orbital (HMO) theory from the assumption that a cyclic conjugated system is aromatic if it contains a closed shell of electrons (Hückel 1938). This rule applies only to monocyclic systems (Hückel 1938, Inagaki and Hirayashi 1977, Mukherjee 1986). It has been extended to annulenes containing one heteroatom (Gutman and Mukherjee 1988). The extension to polycyclic systems is not so successful, however (Goldstein 1967, Balaban 1972, Kruszewski and Krygowski 1975). Instead, various topological rules for polycyclics have been worked out (Balaban 1970, Gutman and Trinajstić 1976, Knop *et al.* 1976). It is worth mentioning that an early box potential model (constant finite potential inside a box and infinite potential outside the box) led to a peripheral model for predicting aromaticity of polycyclics (Platt 1954). The peripheral model asserts that conjugated hydrocarbons are aromatic for which the perimeter and all inner-perimeters (perimeter after eliminating outer perimeters) are connected unbranched even-membered loops with $2(2m+1)$ carbons, except the innermost perimeter which may be a connected unbranched even-membered chain with $2n$ carbons. This model has limited application.

Sometimes present in benzenoid compounds is a loop called the 'aromatic sextet', which is defined as a six electron group which resists disruption, introduced by Armit and Robinson (1925), see also, Robinson (1967). The presence of aromatic sextets stabilizes benzenoid compounds (Robinson 1967, Clar 1964).

The existence of a classical Kekulé structure is a condition for a conjugated molecule to be stable. The number of Kekulé structures K for a molecule without $4n$ rings is given by $K^2 = |a_N|$, where a_N is the value of the HMO secular polynomial with the variable set equal to zero (Dewar and Longuet-Higgins 1952, Graovac *et al.* 1972). $|a_N|$ is an often used stability criterion. Big $|a_N|$ implies large stability (Wilcox 1969, Gutman *et al.* 1975, Swinborne-Sheldrake *et al.* 1975).

Julg and François (1967) introduced an index of aromaticity based on the degree of uniformization of the peripheral bond lengths—the more uniform, the more aromatic. This index is still used because of its easy access (see, for example, Skancke and Skancke (1988)). To emphasize the importance of bond alternation in discussing aromaticity, Binsch *et al.* introduced a criterion based on the theory of double bond fixation, which uses the Taylor series for the total energy in terms of bond distortions (Binsch and Tamir 1969, Binsch 1971). For example, the first-order double-bond fixation is the deviation of the optimized C–C bond length (minimize the energy of Taylor series truncated to the first order) from an ideal C–C bond length. A conjugated π-electron system is called aromatic if it shows neither strong first-order nor second-order double-bond fixation (Binsch and Tamir 1969). Also related to bond alternation is the index defined by peripheral bond orders (Kemula and Krygowski 1968). This index is closely related to Julg's index because of the well-known bond length–bond order correlation (Kemula and Krygowski 1968, Kruszewski and Krygowski 1972a,b). The statistical evaluation of the deviation in peripheral bond orders or peripheral bond lengths provides another index of aromaticity (Bird 1985, 1986, 1987, 1990). An information-theoretic index of aromaticity also has been introduced (Karadakov *et al.* 1981, Fratev *et al.* 1982).

A minimum energy loss in changing one of the conjugating carbons from sp^2 hybridization to sp^3 hybridization facilitates an addition reaction. Hence it can provide a scale of aromaticity based on dynamic behaviour (Kruszewski and Krygowski 1970, 1972a, b, Krygowski 1970).

The localized molecular orbital (LMO) theory provides a framework for discussion of aromaticity. Since any single determinant closed-shell molecular orbital wavefunction is invariant under a unitary transformation of the occupied molecular orbitals, localized molecular orbitals can be defined so that they satisfy some criteria such as maximizing the intraorbital Coulombic repulsion energy and minimizing the interorbital Coulombic repulsion energy and interorbital exchange repulsion energy. Physical observables like total energy and total repulsion energy are unchanged under this kind of transformation (see, for example, Edmiston and Ruedenberg (1963)). A theoretical *RE* can be easily defined within this LMO theory (England and Ruedenberg 1971, England 1975, Kleier *et al.* 1975, Náray-Szabó 1980). Hence

$$RE=\sum(\eta_i-\epsilon_{\mathrm{Et}}),$$

where η_i is the orbital energy of the ith localized πMO, ϵ_{Et} is the π-orbital energy of ethylene, and the summation is over all occupied orbitals (England and Ruedenberg 1971). This definition of *RE* does not take away the contribution from polyenic declocalization. Recently, the lowest πLMO energy has been used to characterize aromaticity. The index invented is: $\Delta\epsilon_{\pi\mathrm{L}}=\epsilon_{\pi\mathrm{L}}(\mathrm{MO})-\epsilon_{\pi\mathrm{L}}(\mathrm{LMO})$, where $\epsilon_{\pi\mathrm{L}}(\mathrm{MO})$ is the lowest eigenvalue of canonical delocalized π molecular orbitals and $\epsilon_{\pi\mathrm{L}}(\mathrm{LMO})$ is the lowest LMO energy (Friedman and Ferris (1990), see also Kollmar (1979)). $\Delta\epsilon_{\pi\mathrm{L}}$ more negative means the compound concerned is more aromatic. This index has only been applied to five-membered heteroconjugated molecules (Friedman and Ferris 1990). Other molecular orbital theories can also be used to describe aromaticity. For example, Sardella (1977) employed perturbational molecular orbital theory to qualitatively access why aromatic molecules are aromatic from the *RE* point of view. Hobey (1972, 1973), on the other hand, used a free electron molecular orbital model to calculate *RE*. Both Sardella and Hobey confirmed the $4n+2$ rule using their methods.

Other models, for example, the Cooper pair model, the passive electron pair model, and the polygonal H_n model have been developed for describing aromaticity (Ichikawa 1983, Schipper 1987, Squire 1987). These models are successful in some respects, but there is controversy about them (Haddon *et al.* 1984, Ichikawa 1984, Squire 1988, van Hooydonk 1988).

Most of the more recent efforts in quantifying aromaticity start from consideration of the thermodynamic stability of aromatic compounds. Dewar and de Llano's recalculation of *RE*, based on the definition of Mulliken and Parr, began a new era in the theory of aromaticity (Mulliken and Parr 1951, Dewar and de Llano 1969). This theory takes all acyclic contributions away from the total energy by using an acyclic reference structure (Dewar and de Llano 1969, Hess and Schaad 1971a, Herndon 1973, Aihara 1976, Randić 1976, Gutman *et al.* 1977). The resulting *RE* is the contribution from the cyclic conjugation. Hence, the bigger this *RE* is, the more aromatic the molecule is. The antiaromaticity is associated with negative *RE* values, which corresponds to a situation for which cyclic conjugation destabilizes the molecule. This is what antiaromaticity means (Bauld *et al.* 1978). The relative hardness index (η_r) introduced by Zhou and Parr (1989) has the same merit (see below).

Recent developments in the theory of aromaticity may be listed as follows: (i) resonance energy (*DRE*) by Dewar and de Llano (1969); (ii) resonance energy (*RE*(*HS*)) by Hess and Schaad (1971a); (iii) topological resonance energy (*TRE*) by Aihara (1976) and Gutman *et al.* (1977); (iv) valence bond structure-resonance theory by Herndon

(1973); (v) conjugated circuits method by Randic (1976); (vi) bond-order approach to ring current by Jug (1983); (vii) absolute and relative hardness criteria by Zhou, Parr and Garst (1988) and by Zhou and Parr (1989). We discuss these in turn, in some detail.

3.1. DRE

Dewar and coworkers showed that bonds in classical polyenes can be regarded as localized (Dewar and Gleicher 1965). The 'polyene' bond energies, which are found to be essentially constant from molecule to molecule, are (Dewar and de Llano 1969)

$$E_{\mathrm{C-C}}=4{\cdot}3499\,\mathrm{eV}, \qquad E_{\mathrm{C=C}}=5{\cdot}5378\,\mathrm{eV}. \tag{2}$$

These results were obtained using a modified version of the Pariser–Parr–Pople (PPP) method (Pariser and Parr 1953, Pople 1953, Dewar and de Llano 1969). The *DRE* was defined as (Dewar and de Llano 1969)

$$DRE=E_a-(n_1E_{\mathrm{C-C}}+n_2E_{\mathrm{C=C}}+n_3E_{\mathrm{C-H}}), \tag{3}$$

where E_a is the heat of atomization of the conjugated molecule concerned, $E_{\mathrm{C-H}}=4{\cdot}4375$ eV is the bond energy of the C–H bond, and n_1, n_2, and n_3 are respectively the numbers of C–C bonds, C=C bonds, and C–H bonds. This scheme is easily extended to molecules containing heteroatoms (Trinajstić 1971). The *DRE* has widely been used as a criterion of aromaticity (Dewar and Trinajstić 1969a, b, Zambelli and Trinajstić 1971, DasGupta and DasGupta 1975).

Efforts have been made to derive Dewar-type parameters for the localized reference structure within HMO theory (Figeys 1970a, b, Milun *et al.* 1972, Gutman *et al.* 1973, Sharma 1978, Tewari and Srivastava 1988). They are partially successful. The perturbation molecular orbital (PMO) technique can furnish easy and reasonable estimates of Dewar resonance energies (Dewar and Dougherty 1975, Durkin and Langler 1987).

3.2. RE(HS)

Instead of using only two parameters for single and double bond energies, as Dewar and coworkers did, Hess and Schaad introduced eight parameters based on their simple HMO calculations (Hess and Schaad 1971a). They argued that the 'polyene' bond energy depends not only on the bond type, but also on the bonding status of the terminal carbon atoms comprising the bond. The parameters they obtained are listed in table 2 (Schmalz *et al.* 1987).

The definition of *RE*(*HS*) is similar to the definition of *DRE*—with an opposite sign convention

$$RE(HS)=E_\pi-\sum_i n_iE_i, \tag{4}$$

where E_π is the total (HMO) π energy of the molecule, n_i is the number of *i*-type bonds, and E_i is the bond energy parameter for bond of type *i*. Equation (4) is readily

Table 2. Bond types and bond energies (in β) for acyclic polyenes.†

Bond type	Bond energy	Bond type	Bond energy
$H_2C{=}CH$	2·0000	C=C	2·1734
HC=CH	2·0710	HC–CH	0·4649
$H_2C{=}C$	2·0000	HC–C	0·4356
HC=C	2·1101	C–C	0·4359

† Units are β, the basic resonance integral of the HMO method.

generalized to heteroconjugated molecules (Hess *et al.* 1972, 1975, Hess and Schaad 1973). Hess and Schaad showed that the resonance energy per π electron (*REPE*) is still more useful when comparing stabilities for different molecules (Hess and Schaad 1971a, b, c).

Several reparametrization schemes have been developed. One is based on graph theory, which involves only five parameters (Jiang *et al.* 1984). The others employs a 'cluster expansion' technique (Schmalz *et al.* 1987). Some improved results are obtained. The ω-technique, which calculates Coulomb integral self-consistently, also has been invoked to calculate the total π-energy in an effort to improve the *RE*(*HS*) result (Castro and Fernádez 1983).

3.3. TRE

In graph-theoretic molecular orbital theory, the coefficients of the HMO secular polynomial $P(G,x)$ for a conjugated molecule can be divided into two parts: the first containing the contributions from the cycles of the molecular graph G, the second comprising all other contributions. Aihara (1976), and Gutman *et al.* (1977) argued that for a cyclic conjugated molecule if there were no cycles the coefficients of the HMO secular polynomial would be only the second part of the above. Hence a hypothetical acyclic reference structure can be defined in such a way that its secular polynomial $P^{ac}(G,x)$ has the same form as $P(G,x)$ with the coefficients being just those of the second part. Let $\{x_i\}_{i=1}^{N}$ and $\{x_i^{ac}\}_{i=1}^{N}$ be the roots of $P(G,x)$ and $P^{ac}(G,z)$ respectively. Then *TRE* is

$$TRE=\beta\sum_{i,\text{occ.}}(x_i-x_i^{ac}). \tag{5}$$

The value of *TRE* depends only on the topology of the molecule. The definition of equation (5) is parameter-free. Its extension to heteroconjugated molecule is automatic. Again *TRE* per π electron (*TREPE*) is useful in comparison among molecules. It is routine, but tedious particularly for large molecules, to obtain $P^{ac}(G,x)$ (Gutman *et al.* 1977). Techniques have been developed to derive $P^{ac}(G,x)$ from graph theory (see, for example, Trinajstić (1983), Hosoya (1986)). The roots of $P^{ac}(G,x)$ fortunately are real (Heilmann and Lieb 1972, Gutman 1981, Trinajstić 1983).

There are difficulties with *TRE* regarding the existence of a classical acyclic structure corresponding to the acyclic polynomial $P^{ac}(G,x)$ (Gutman 1979, Gutman and Mohar 1980, 1981, Heilbronner 1982).

A new topological resonance energy has recently been introduced using the properties of molecular graphs and their fragments (Jiang and Zhang 1989, 1990, Jiang *et al.* 1989). This newly defined *TRE* is similar but not completely equivalent to the old *TRE* (Gutman *et al.* 1989).

3.4. *Valence bond structure* RE

Herndon's valence bond (VB) structure resonance theory is a crude VB model which considers only the contributions from Kekulé structures (Herndon 1973). The wavefunction Ψ is assumed to be a simple sum of wavefunctions $\{\psi_i\}_{i=1}^{N}$ corresponding to N Kekulé structures with equal coefficients, namely

$$\Psi=\sum_{i=1}^{N}\frac{\psi_i}{\sqrt{N}}. \tag{6}$$

Then the resonance energy is defined as

$$RE=E[\Psi]-\sum_{i=1}^{N}\frac{E[\psi_i]}{N}=2\sum_{i>j}^{N}\frac{H_{ij}}{N}, \tag{7}$$

with

$$E[\Phi]=\int\Phi\hat{H}\Phi\,\mathrm{d}\tau, \tag{8}$$

$$H_{ij}=\int\psi_i\hat{H}\psi_j\,\mathrm{d}\tau, \tag{9}$$

where $\hat{H}$ is the Hamiltonian of the molecule. Note that $E[\psi_i]$ is the molecular energy with the localized single and double bonds of the ith Kekulé structure. The values of H_{ij} are determined empirically (Herndon 1973, 1983, Herndon and Ellzey 1974, Herndon and Agranat 1983).

Improved VB models have also been applied to the problem of aromaticity (van der Hart *et al.* 1972, Epiotis 1983, Kuwajima 1984). They are much more complicated and less successful than Herndon's model and the model of Randić we are going to describe next.

3.5. *Conjugated circuit model*

In a conjugated molecule a cycle is called a conjugated circuit if it consists of a even number of bonds Randić argues that a $4n$-conjugated circuit in a conjugated molecule should destabilize the molecule while a $4n+2$-circuit should stabilize it. He further demonstrates that the resonance energy can be considered as the total contribution from all conjugated circuits of the molecule (Randić 1976, 1977, Randić *et al.* 1989)

$$RE=\sum_{n=1}(M_nR_n+N_nQ_n), \tag{10}$$

where M_n and N_n are the numbers of the conjugated circuits with ring sizes $4n+2$ and $4n$ in the molecule, respectively, and the parameters R_n and Q_n are respectively the contributions to RE of individual $4n+2$ and $4n$ circuits. Even for big molecules the summation in equation (10) does not require more than three or four terms since $|R_n|$ and $|Q_n|$ are very small numbers for $n>4$. The parameters R_n and Q_n are empirically determined. The extension to molecules containing heteroatoms has been made (Randić *et al.* 1988).

Randić's RE model is different from Herndon's VB structure resonance theory, though they give similar predictions (Schaad and Hess 1982). With suitable truncation of equation (10) and with careful reparametrization of R_n's and Q_n's we can get the same numerical values of Herndon's VB resonance theory from the conjugated circuit model (Randić 1976).

3.6. *Ring current criterion*

Starting from the fact that theoretical bond orders should be invariant under a unitary transformation of atomic orbital basis set used, Jug defined the maximum one among all possible unitary transformations as the bond order (Jug 1977). He argued that the magnitude of ring current around a ring must be determined by the bond of minimum bond order in the ring. He then defined this minimum bond order as the aromatic index (Jug 1983). For a polycyclic molecule only peripheral bonds count. Jug's criterion gives good predictions for the molecules discussed, though the number of these was limited.

3.7. *Hardness* (η) *and relative hardness* (η_r) *criteria*

Hardness is approximately $(I-A)/2$ or half the gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) if a molecular orbital theory is used (Parr and Pearson 1983, Pearson 1986). I and A are respectively the ionization potential and electron affinity. Relative hardness is defined as $\eta_r = \eta - \eta_a$, where η_a is the hardness of the same hypothetical acyclic reference structure as is used in the definition of *TRE* (Zhou and Parr 1989). Both η and η_r have been shown to be good measures of aromaticity, and η can be calculated at different level of sophistication (Zhou *et al.* 1988, Zhou and Parr 1989, Zhou and Navangul 1990). The fact that η and η_r can measure aromaticity was important in the discovery of a principle of maximum hardness (Pearson 1987, Zhou and Parr 1989, 1990, Zhou 1990, Parr and Chattaraj 1991). For a metal, 2η is the reciprocal of the total density of states at the Fermi level (Yang and Parr 1985).

Before η and η_r were used as criteria of aromaticity, the HOMO, LUMO energies and their difference already had been connected with the concept of aromaticity in several different ways. For example, small HOMO–LUMO gap had been associated with antiaromaticity for some molecules (Cava and Mitchell 1967, Dewar 1971a, b, Vollhardt 1975, Vollhardt and Yee 1977, Willner and Rabinovitz 1980, Minsky *et al.* 1985a, Minsky *et al.* 1985b, Cohen *et al.* 1986, Cohen *et al.* 1987, Budzelaar *et al.* 1987). And stabilities of some species have been attributed to large gaps (Mihart *et al.* 1983, Minot 1987). The number of Kekulé structures for a molecule has been connected with HOMO–LUMO gap (Cioslowski and Polansky 1988). HOMO and LUMO bonding types have been used as indicators of aromaticity (Sinanoğlu 1988a, b).

3.8. *Unified theories*

Some measures of aromaticity clearly take more than one aspect of the concept of aromaticity into consideration. Haddon and Fukunaga showed that for $(4n+2)$annulenes *RE*, which measure the thermodynamic stability of the molecule, is connected to the ring current in a very simple way (Haddon 1979, Haddon and Fukunaga 1980). Similar relationships also hold between *RE* and other ring current-related quantities (Verbruggen 1982, Mizoguchi 1984).

The hardness, first introduced as an index of reactivity (Pearson 1973, 1986, Parr and Pearson 1983), unifies all three main aspects of aromaticity. Take the diamagnetic

Table 3. Numerical values of aromaticity indices for benzene (C_6H_6), cyclobutadiene (C_4H_4), and buckmisterfullerene (C_{60}).

	C_6H_6	C_4H_4	C_{60}
η	$-1\cdot0\,\beta^{(a)}$	$0\,\beta^{(a)}$	$-0\cdot378\,\beta$
η_r	$-0\cdot482\,\beta^{(a)}$	$0\cdot765\,\beta^{(a)}$	$-0\cdot316\,\beta$
REPE(*HS*)	$0\cdot065\,\beta^{(b)}$	$-0\cdot268\,\beta^{(b)}$	$0\cdot031\,\beta^{(c)}$
TREPE	$0\cdot046\,\beta^{(d)}$	$-0\cdot307\,\beta^{(d)}$	$0\cdot0274\,\beta^{(e)}$
DREPE	$21\,\mathrm{kcal\,mol^{-1\,(f)}}$	$-17\,\mathrm{kcal\,mol^{-1\,(f)}}$	
REPE (Herndon)	$0\cdot14\,\mathrm{eV}^{(g)}$	$-0\cdot16\,\mathrm{eV}^{(g)}$	$0\cdot12\,\mathrm{eV}^{(c)}$
REPE (Randić)	$0\cdot145\,\mathrm{eV}^{(h)}$	$-0\cdot400\,\mathrm{eV}^{(h)}$	$0\cdot116\,\mathrm{eV}^{(i)}$
Jug index	$1\cdot751^{(j)}$	$0\cdot980^{(j)}$	

References are: (*a*) Zhou and Parr 1989; (*b*) Hess and Schaad 1971a; (*c*) Klein *et al.* 1986; (*d*) Gutman *et al.* 1977; (*e*) Aihara *et al.* 1988; (*f*) Baird 1971; (*g*) Herndon and Ellzey 1974; (*h*) Randić and Trinajstić 1984; (*i*) Truncated at $n=2$ in equation (10) of the text with $R_1 = 0\cdot869$ eV and $R_2 = 0\cdot246$ eV; (*j*) Jug 1983.

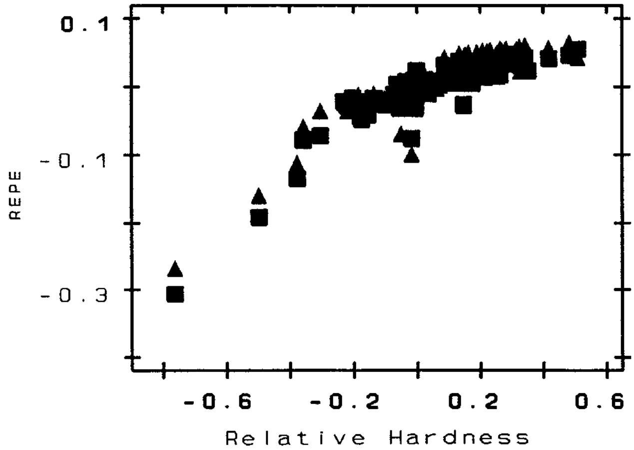

Figure 2. Correlation of relative hardness (in β) with *REPE*(*HS*) (in β, ▲) and *TREPE* (in β, ■). Data are from a paper by Zhou and Parr (1989).

susceptibility χ, which is a induced ring current related quantity, as an example. The Unsöld approximation to the second term in equation (1), which takes all denominators outside the summation (Unsöld 1927), gives a denominator of a common energy gap which is roughly proportional to the absolute hardness. Hence the absolute hardness can measure the induced ring current effects in cyclic conjugated molecules. Accordingly, aromaticity is a property parallel to hardness. Note also that the same sort of second-order perturbation formula enters various theories of reactivity (see, for example, Levine (1969), Fukui (1975)); again the Unsöld approximation produces the relation to hardness.

To conclude this section we give in table 3 values of different indices for benzene (C_6H_6), cyclobutadiene (C_4H_4), and buckmisterfullerene (C_{60}). All indices predict that C_{60} is aromatic. In figure 2 we show how relative hardness correlated with *TREPE* and *REPE*(*HS*) for a set of molecules (data are from Zhou and Parr (1989)).

4. Conclusions

We have tried here to survey theoretical viewpoints of aromaticity. No attempts have been made to detail experimental approaches to the problem. Other aspects we have not touched are: applications of the theories and non-classical aromaticity (cyclic conjugation other than pπ interaction of classical multiple bonds). Non-classical aromaticity, like homoaromaticity, σ-aromaticity, superaromaticity (reference structures used are aromatic themselves) (Cioslowski *et al.* 1991), and three-dimensional aromaticity, is a big topic, to which most of the techniques and theoretical models described in the previous Section are applicable.

Resonance energy is a valence bond theory concept; band gap is a molecular orbital concept. Our own conclusion is that *RE* per electron is a good measure of aromaticity in the valence-bond language, band gap an equally good (or better?) measure in the molecular orbital language. And we call attention to the broad applicability of the band gap concept, like MO theory, through all of chemistry (organic and inorganic) and through solid-state and surface chemistry and physics.

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