Bond resonance energies of polycyclic benzenoid and non-benzenoid hydrocarbons

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The bond resonance energy represents the contribution of a given π bond in a molecule to the topological resonance energy. Bond resonance energies for 43 typical polycyclic conjugated hydrocarbons and five of their molecular ions have been evaluated and critically examined. Polycyclic benzenoid hydrocarbons do not have π bonds with negative bond resonance energies. For every benzenoid hydrocarbon, relative magnitudes of the bond resonance energies reflect the locations of aromatic sextets in the Clar structure. A molecule is predicted to be chemically very reactive if it has one or more π bonds with large negative bond resonance energies. Many non-benzenoid hydrocarbons are kinetically unstable in this sense. All anti-aromatic hydrocarbons have one or more π bonds with large negative bond resonance energies. This bond resonance energy model can be used to explore the utility and the limitations of the conjugated-circuit theory developed by Herndon, Randić and Gomes. Except for azulene, Platt's perimeter model is not compatible with the relative magnitudes of the bond resonance energies in a molecule.

Physical and chemical properties inherent in aromatic molecules have been referred to collectively as aromaticity.[1-3] The first successful definition of aromaticity was the one based on the so-called Dewar resonance energy. In 1965 Dewar and co-workers defined the Dewar resonance energy as a stabilization energy due solely to cyclic conjugation.[4-6] In 1971 Hess and Schaad reported that the Dewar-type resonance energy can be defined within the framework of Hückel molecular orbital (HMO) theory.[7-9] We then found that the Dewar-type resonance energy can be defined by graph theory using HMO theory.[10-13] Stabilization energy defined in this manner has been called topological resonance energy, and has been used as one of the practical indices for determining the degree of aromaticity. Positive Dewar and topological resonance energies are associated with aromaticity, whereas negative Dewar and topological resonance energies are associated with anti-aromaticity.

In chemical graph theory, the term 'circuit' means a cyclic path which can be chosen from a cyclic conjugated system.[14,15] Aromaticity and anti-aromaticity arise from all possible circuits in a conjugated system. Hosoya *et al.*,[16] Aihara,[17] Herndon,[18,19] Randić[20,21] and Gomes[22] extensively studied such a geometric aspect of aromaticity. Herndon and Randić's conjugated-circuit model successfully reproduces Dewar resonance energies of many polycyclic conjugated systems.[18-22] Such reproducibility of Dewar resonance energies constitutes semi-empirical evidence for the existence of a relationship between aromaticity and local ring structures in the molecule. Hosoya's graph-theoretical analysis of the π-binding energy is consistent with the definition of the topological resonance energy.[16,17] However, a possible relationship between chemical reactivity and aromaticity has never been investigated thoroughly.

We previously formulated the bond resonance energy by graph theory, which represents the contribution of a given π bond to the topological resonance energy.[23-25] A π bond with a large negative bond resonance energy is presumed to be anti-aromatic at least around there. Just as a highly anti-aromatic molecule is very reactive,[4-12] a molecule with a highly anti-aromatic local structure must be very reactive and fragile. We first applied the bond resonance energy method to fullerenes, and found that fullerenes with abutting pentagons have one or more π bonds with large negative bond resonance energies.[23] Thus, calculated bond resonance energies were consistent with the isolated pentagon rule (IPR).[26,27] The IPR holds for neutral fullerene molecules, but not for their molecular ions.[24] All fullerenes isolated so far are IPR fullerenes without highly anti-aromatic π bonds.

In this paper, we show that the bond resonance energy method can be utilized to analyse the origin of aromaticity and the possible relationship between chemical reactivity and molecular geometry for planar polycylic benzenoid and non-benzenoid hydrocarbons. Remember that Dewar and topological resonance energies represent thermodynamic stability of an entire molecule, whereas the bond resonance energy and chemical reactivity are closely associated with a local structure in a molecule.[23-25] The present method is also useful for critically testing the conjugated-circuit model,[18-22] Clar's structural formulae[28,29] and Platt's perimeter model[30,31] for polycyclic conjugated systems.

Theory

Aromaticity and the chemical reactivity of polycyclic conjugated hydrocarbons are determined primarily by π electrons since high-lying molecular orbitals are formed by $2p_Z$ atomic orbitals. Therefore, these properties can in principle be analysed in terms of HMO theory. In line with this, the topological resonance energy is defined using simple HMO theory.[10-13] The percentage topological resonance energy is useful when one wants to compare the degrees of aromaticity in different molecules.[13,23,24] It is defined as 100 times the topological resonance energy, divided by the total π-binding energy of the polyene reference, a hypothetical polyene-like reference structure used to evaluate the topological resonance energy.[10-13] Thus, the percentage topological resonance energy is an aromatic stabilization energy of the molecule, normalized to the total π-binding energy of the polyene reference. It will be referred to simply as a percentage resonance energy.

To define the bond resonance energy,[23] a secular equation is first written for a given molecule with a total π-binding energy E_0. Then, one of the two off-diagonal elements corresponding to an arbitrarily chosen π bond in the molecule, *e.g.* the C_p–C_q bond, is multiplied by *i*, and the other by −*i*, where *i* is the square root of −1.[32,33] All other elements in the determinant are kept unchanged. The total π-binding energy obtained by solving this modified secular equation is denoted by E_{pq}, which is devoid of aromatic stabilization due to the circuits sharing the C_p–C_q bond. In other words, E_{pq} is the total π-binding energy of the molecule in which the C_p–C_q bond alone is made artificially olefinic. Hence, the difference between E_0 and E_{pq} can be interpreted as the contribution of the C_p–C_q bond to aromaticity, so may be called the bond resonance energy for the C_p–C_q bond.[23] The sum of bond resonance energies over all π bonds is not equal to the topological resonance energy. In the case of monocyclic systems, all the bond resonance energies are equal to the topological resonance energy.

Results and discussion

Benzenoid hydrocarbons

The bond resonance energies and the π-bond orders for all non-identical π bonds for typical benzenoid hydrocarbons **1–17** are given in Fig. 1. The topological resonance energies (E_{tr}s)

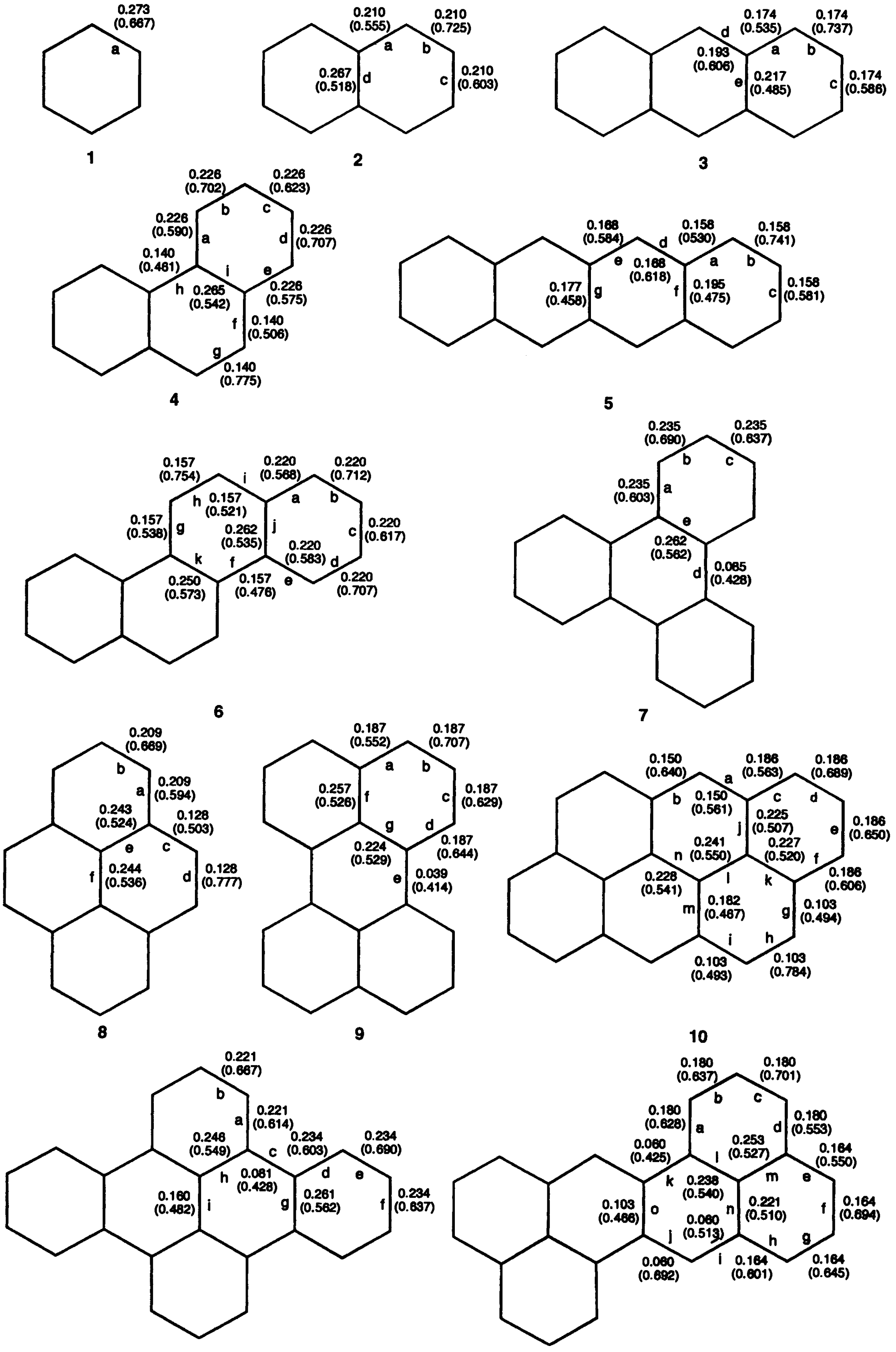
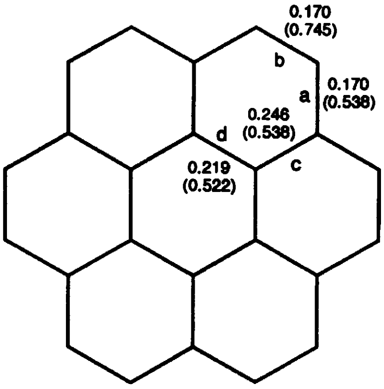


Fig. 1 Bond resonance energies for polycyclic conjugated benzenoid hydrocarbons 1–17. Values in parentheses are π-bond orders.

and the percentage topological resonance energies (%E_{tr}s) for the benzenoid class of hydrocarbons **1–17** are listed in Table 1. All these benzenoid systems are highly aromatic with large positive percentage resonance energies. Since there are no π bonds with negative bond resonance energies, these molecules are kinetically more stable or chemically more inert than their polyene references. All C–C bonds in **1–17** contribute more or less to the aromaticity in the molecule. However, all the bond resonance energies are smaller than that of benzene (**1**). It then follows that the conjugated system of any polycyclic



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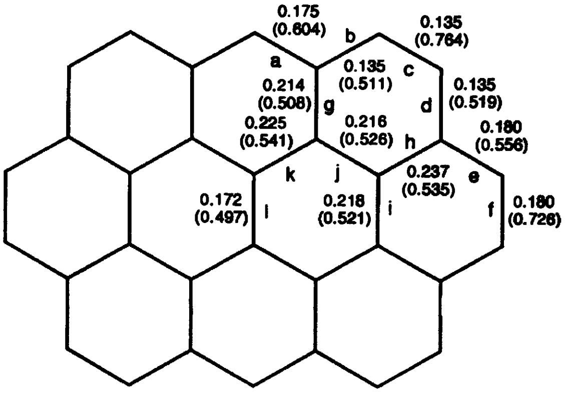

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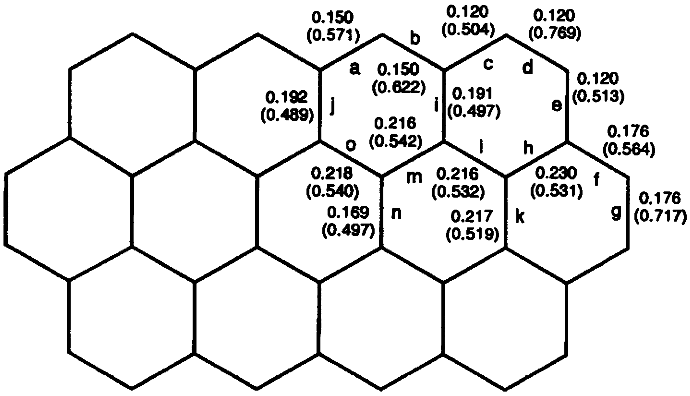

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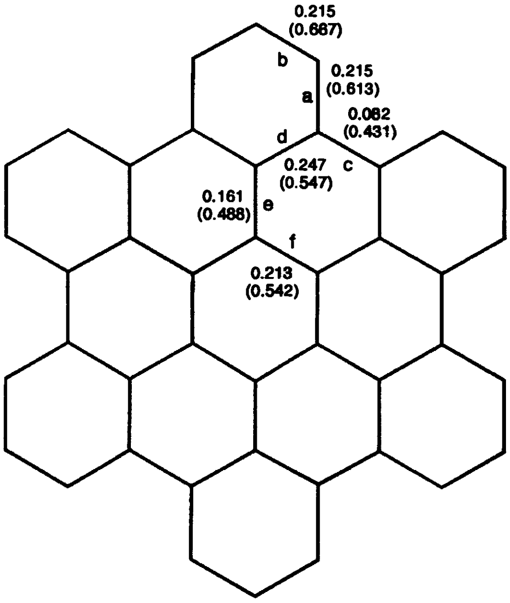

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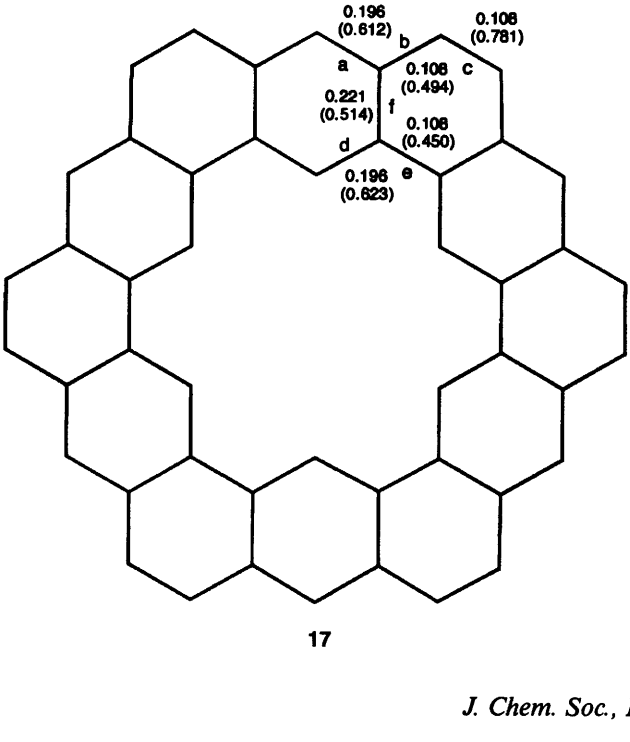

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Table 1 Topological and percentage resonance energies for polycyclic benzenoid hydrocarbons

Species	$E_{tr}/\|\beta\|$	$\%E_{tr}$
Benzene (**1**)	0.273	3.53
Naphthalene (**2**)	0.389	2.92
Anthracene (**3**)	0.475	2.52
Phenanthrene (**4**)	0.546	2.89
Naphthacene (**5**)	0.553	2.27
Chrysene (**6**)	0.688	2.81
Triphenylene (**7**)	0.739	3.01
Pyrene (**8**)	0.598	2.73
Perylene (**9**)	0.740	2.69
Dibenzo[*def,mno*]chrysene (**10**)	0.766	2.51
Dibenzo[*fg,op*]naphthacene (**11**)	0.983	2.96
Dibenzo[*hi,qr*]naphthacene (**12**)	0.780	2.36
Coronene (**13**)	0.947	2.82
Ovalene (**14**)	1.224	2.70
Circumanthracene (**15**)	1.476	2.59
Hexabenzo[*bc,ef,hi,kl,no,qr*]coronene (**16**)	1.739	2.92
Kekulene (**17**)	1.569	2.34

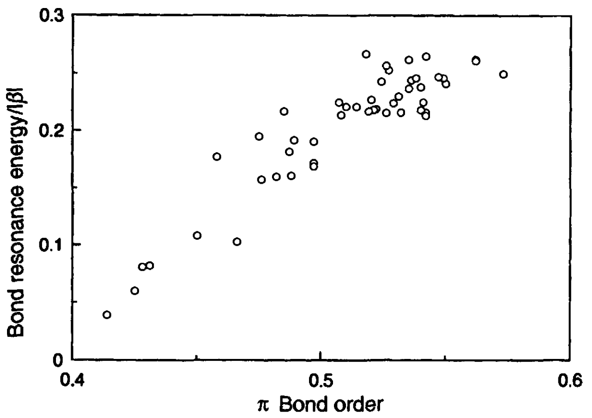


Fig. 2 Bond resonance energies *versus* π bond orders for benzenoid hydrocarbons

benzenoid hydrocarbon is kinetically less stable than that of **1**.

Let C–C bonds in polycyclic conjugated hydrocarbons be classified as two types according to the number of hydrogen atoms attached to each C–C bond. Type-I bonds are the C–C bonds to which no hydrogen atoms are attached. These are not only π bonds located inside the periphery of the molecule, but also such peripheral bonds as bond h in phenanthrene (**4**) and bond f in chrysene (**6**). Type-II bonds are all C–C bonds to which one or two hydrogen atoms are attached. Therefore, all type-II bonds are located along the periphery of the molecule.

As shown in Fig. 2, a fairly good correlation is found between the bond resonance energies and the π bond orders for type-I C–C bonds of benzenoid hydrocarbons. We might say that such a correlation holds because both quantities are related in one way or another to the strength of the π bond. However, a similar correlation is not observable for type-II C–C bonds. When some type-II bonds are located along the same ring in a given molecule, they necessarily have the same bond resonance energy, but have very different π-bond orders. This implies that bond-length alternation or something similar is introduced along the periphery of the conjugated system. Most π bonds shared by two hexagons are more aromatic than peripheral π bonds.

Relative magnitudes of bond resonance energies within a given molecule can be rationalized qualitatively in terms of the conjugated-circuit theory.[18–22] A C–C bond shared by *m*- and *n*-membered rings is denoted by an *m*/*n* bond. When one of the 6/6 bonds in a polycyclic benzenoid hydrocarbon is made olefinic artificially, two six-membered conjugated circuits are usually lost. As six-membered conjugated circuits are highly aromatic in nature,[18–22] the loss of two six-membered circuits must result in a large decrease in aromaticity. It is primarily for this reason that most 6/6 bonds have large positive bond resonance energies. When a 6/6 bond is made olefinic, some 10- and 14-membered conjugated circuits are also lost, which are aromatic to a lesser extent. However, when a peripheral bond is made olefinic, at most one six-membered conjugated circuit, together with one or more 10-membered conjugated circuits, is lost. This leads to a relatively small decrease in aromaticity.

For example, all π bonds in naphthalene (**2**) and anthracene (**3**) are aromatic with large or very large positive bond resonance energies, which support the fact that all these C–C bonds participate in the formation of aromatic conjugated circuits. Bonds a, b and c in **2** and **3** and bond d in **3** are aromatic since they are shared by one six-membered and one or two 10-membered conjugated circuits. Bond d in **2** has the largest bond resonance energy because it is a 6/6 bond. The same is true of bond e in **3** and many 6/6 bonds in other benzenoid hydrocarbons. It is presumably worth emphasizing that this aspect of benzenoid hydrocarbons cannot be predicted from the relative magnitudes of π-bond orders. π-Bond orders of 6/6 bonds are usually smaller than those of peripheral π bonds.

Perylene (**9**) and dibenzo[*hi,qr*]naphthacene or zethrene (**12**) can be described as a combination of two naphthalene nuclei separated by some fixed single and/or double bonds. Fixed single and/or double bonds in **9** and **12** do not participate in the formation of conjugated circuits. Calculated bond resonance energies are large along the naphthalene nuclei, in harmony with this picture. The topological resonance energy of perylene (0.740 |β|) is slightly smaller than twice that of **2** (0.778 |β|). The topological resonance energy of **12** (0.780 |β|) is comparable to twice that of **2**. These resonance energy values are also in accordance with the above picture.

Relative magnitudes of bond resonance energies in every benzenoid hydrocarbon are also consistent with its Clar structure, in which the maximum number of isolated aromatic sextets are indicated.[28,29] Clar's structural formulae for 17 benzenoid hydrocarbons are presented in Fig. 3. In general, π bonds located along the aromatic sextets have larger positive bond resonance energies than other C–C bonds. For example, there are two aromatic sextets in the Clar structure of **4** (**4**^{C}), which are located at two edge hexagons. C–C bonds located around these hexagons have very large bond resonance energies, contributing much to aromaticity. In contrast, single and double bonds fixed at the periphery of a Clar structure, if any, have very or fairly small bond resonance energies. These aspects of Clar structures are common to all benzenoid hydrocarbons, and can be accounted for qualitatively in terms of the conjugated-circuit theory.[34,35]

For polyacenes and some others, more than one Clar structure can be written. There is only one aromatic sextet in Clar structures of polyacenes, such as **2**^{C}, **3**^{C} and **5**^{C}, regardless of the size of the molecule. The only aromatic sextet can in principle be assigned to any of the constituent hexagonal rings, thus being shared by all of them. Therefore, the very aromatic sextet is diluted in a larger polyacene molecule, so that the bond resonance energies of the peripheral C–C bonds become gradually smaller. The bond resonance energies of the peripheral C–C bonds decrease in the order: **1** > **2** > **3** > **5**. This is the reason why larger polyacenes are much less aromatic.[27] The naphthalene nuclei in **9** and **12** are also a kind of polyacene.

Central rings in **9** and **12**, for example, have been called empty rings since aromatic sextets cannot be placed there.[28,29] The term 'empty rings' is generally acceptable in view of the calculated bond resonance energies. The central ring in **9** is really empty, but two central rings in **12** do not seem to be fully empty. Bond e in **9** and bonds i–k in **12** have reasonably small bond resonance energies. However, bond o in **12** contributes moderately to aromaticity, possibly because it is shared by two hexagonal rings. This cannot be predicted from the conjugated-circuit model.[18–22] Thus, two non-conjugated circuits in **12** appear to contribute slightly to the aromaticity, but its contribution is

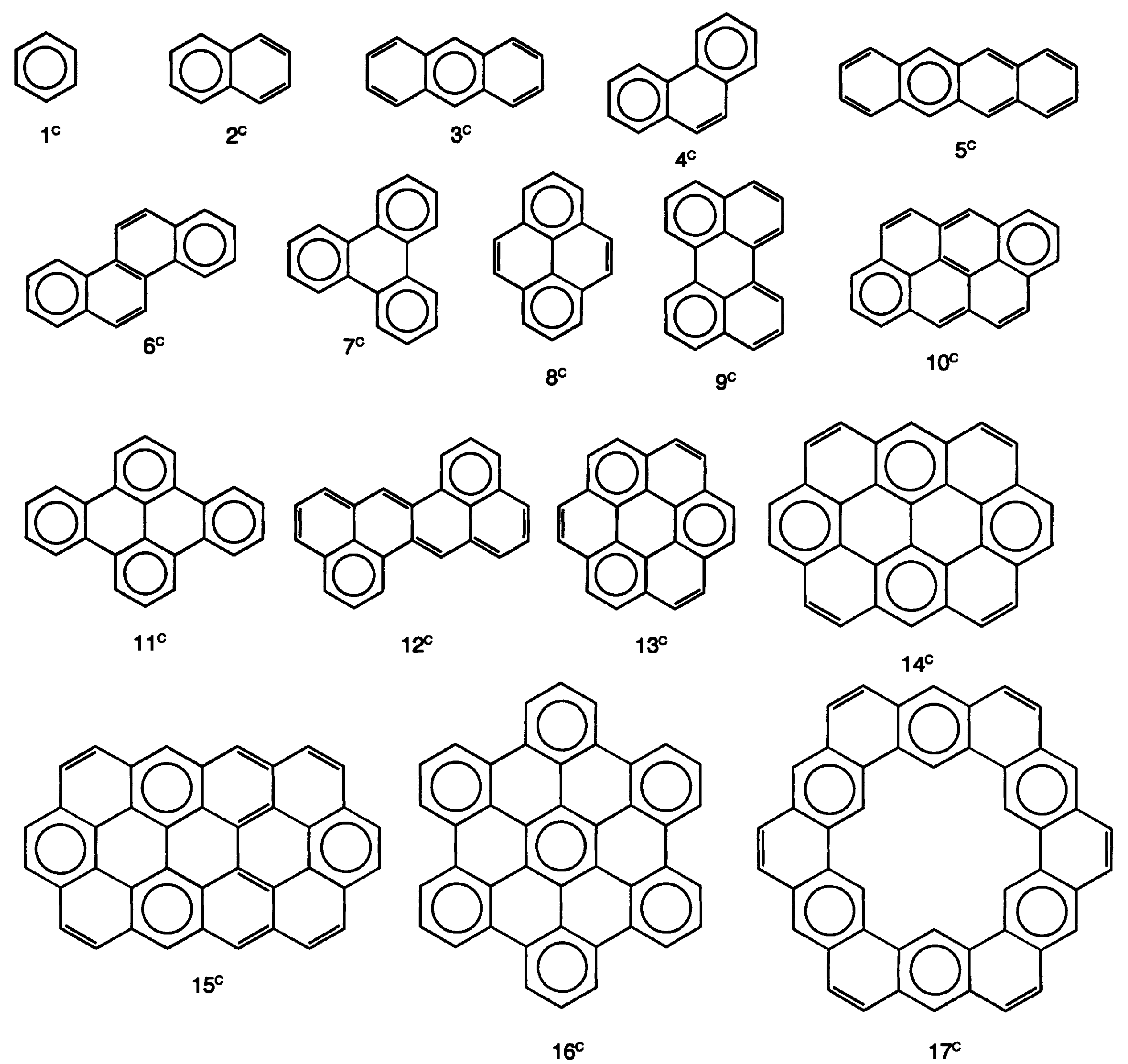


Fig. 3 Clar structures for benzenoid hydrocarbons. Two or more Clar structures can be written for **2**, **3**, **5**, **6**, **9**, **10**, **12**, **13** and **15**.

not large enough to keep the central benzene rings highly aromatic. According to Hosoya's way of reasoning,[16,17] all six-membered circuits contribute more or less to the aromaticity.

Triphenylene (**7**), dibenzo[*fg*,*op*]naphthacene (**11**) and hexabenzo[*bc*,*ef*,*hi*,*kl*,*no*,*qr*]coronene (**16**) are so-called fully benzenoid hydrocarbons, being not only highly aromatic but also kinetically very stable.[28,29] Clar structures of these hydrocarbons consist of aromatic sextets with no formal double bonds. π Bonds located along the aromatic sextets have much larger bond resonance energies than single bonds connecting them. Peripheral single bonds in the Clar structures of fully benzenoid hydrocarbons have very small bond resonance energies although they are not fixed single bonds in the Kekulé structures. Bond d in **7**, bond c in **11** and bond c in **16** are such π bonds. However, when a formal single bond in a Clar structure is shared by two hexagonal rings, it has a moderately large bond resonance energy. It is exemplified by bond i in **11** and bond e in **16**. These bonds are also shared by many larger aromatic conjugated circuits.

Platt once premised that peripheral conjugation primarily determines the degree of aromaticity in a polycyclic conjugated system.[30,31] It was an attempt to extend the Hückel $4n + 2$ rule to polycyclic systems. Many aromatic hydrocarbons may be formed by starting with a cyclic polyene and then by introducing cross-links. If cross-links are regarded as small perturbations, the derived molecules are directly related to the original cyclic polyenes and the Hückel rule may be applied.[31] According to this presumption, **2**, **3** and pyrene (**8**) must be aromatic since their peripheral circuits consist of 10, 14 and 14 carbon atoms, respectively. All catacondensed benzenoid hydrocarbons must be aromatic in this sense.

However, we should note that not only the conjugated-circuit theory,[18–22] but also the present study definitely disprove this perimeter model. As π bonds shared by two six-membered conjugated circuits have large positive bond resonance energies, cross-links in benzenoid hydrocarbons are never small perturbations. Therefore, one cannot say that a peripheral conjugated circuit in any polycyclic benzenoid system determines the major part of aromaticity. Benzenoid hydrocarbons, *e.g.* **2**, **3** and **8**, are never perturbed nor substituted annulenes since cross-links have very large bond resonance energies. To a zeroth-order approximation, all polycyclic benzenoid hydrocarbons should be regarded as two or more benzene rings condensed with each other. The conjugated-circuit theory supports the view that the main origin of aromaticity is individual benzene rings.[18–22]

When bond a, b or c in **2** is made olefinic artificially, it becomes a kind of substituted benzene. Its topological resonance energy was calculated to be 0.179 $|\beta|$, which is smaller by 0.094 $|\beta|$ than unsubstituted benzene (**1**). Likewise, when bond a, b or c in **3** is made olefinic, it becomes a kind of substituted naphthalene, which has two six- and one ten-membered conjugated like unsubstituted naphthalene (**2**). The topological resonance energy of this substituted naphthalene is 0.301 |*β*|, which is 0.088 |*β*| smaller than that of **2**. Smaller resonance energies of such hypothetically substituted benzenoid systems can be justified by remembering that a substituted aromatic molecule in general is less aromatic than the unsubstituted one. When bond d in **3** is made olefinic, the conjugated system becomes two benzene rings combined with two olefinic methine groups. The topological resonance energy of the resulting system is 0.282 |*β*|, which is 0.264 |*β*| smaller than twice that of **1**, but is nearly equal to that of **1**. This hypothetical conjugated system may be viewed as a combination of benzene and essentially non-aromatic *o*-xylylene.

Non-benzenoid hydrocarbons

The bond resonance energies and the π bond orders for all non-identical π bonds for typical non-benzenoid hydrocarbons **18–43** are given in Fig. 4. Topological and percentage resonance

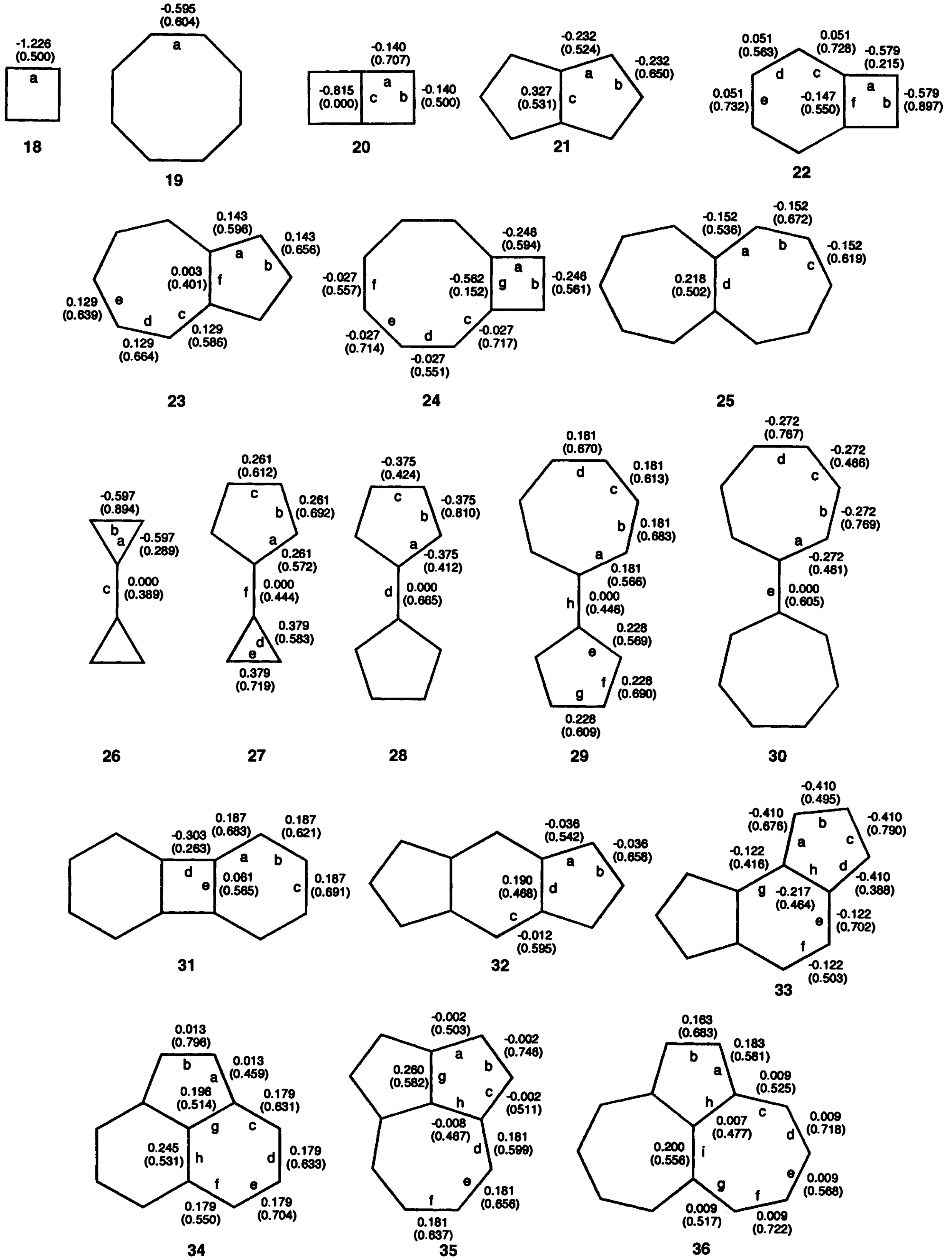


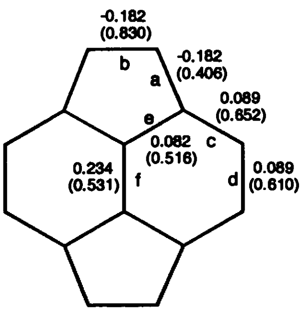
Fig. 4 Bond resonance energies for polycyclic conjugated non-benzenoid hydrocarbons **18–43**. Values in parentheses are π-bond orders.

energies for typical non-benzenoid hydrocarbons **18–43** are listed in Table 2. Topological and bond resonance energies for some non-alternant systems are overestimated due to the use of simple HMO theory. In particular, actual calicene (**27**) and cyclic bicalicene (**40**) must be considerably less aromatic than predicted from the percentage resonance energies. The topological resonance energies calculated using the ω-technique to support this.[36] It is still true that some non-benzenoid hydrocarbons are aromatic with fairly large positive percentage resonance energies, but that some others are highly anti-aromatic with large negative ones.

Fig. 5 shows that there again appears to be a correlation between the bond resonance energies and the π bond orders for type-I bonds. However, the data points in the π bond order >0.4 show a great deal of scatter as compared with those in Fig. 2. This may imply that non-benzenoid or non-alternant conjugated systems have fundamentally different characters from benzenoid ones. Strengths of constituent C–C bonds seem to be interdependent to a considerable extent.

Examination of bond resonance energies for non-benzenoid hydrocarbons revealed that, as in the case of benzenoid systems, π bonds shared by two hexagonal rings contribute much to the aromaticity. These bonds have large π bond orders. Bond h in acenaphthylene (**34**), bond f in pyracylene (**37**), bond k in fluoranthene (**38**), bonds r–v in cyclopental[*cd*]pyrene (**41**), bond c in corannulene (**42**) and bond c in [7]circulene (**43**) are such examples. π Bonds shared not by two six-membered conjugated circuits, but by two or more ten-membered ones may also contribute much to aromaticity. Bonds d, e and f in cyclopent[*cd*]azulene (**35**), bonds a and b in aceheptylene (**36**) and bond f in azupyrene (**39**) are such examples.

Among the non-benzenoid hydrocarbons studied, **34**, **38** and **41** can be classified as semi-benzenoid hydrocarbons since they consist of one or two benzenoid subsystems combined with fixed single and double bonds. These molecules are as highly aromatic with large positive percentage resonance energies as typical benzenoid hydrocarbons.[6,7,9,10–13] However, as in the case of **9** and **12**, bond resonance energies of the essential single and double bonds are very small. Five-membered rings in these molecules are empty in Clar's sense.[28,29]



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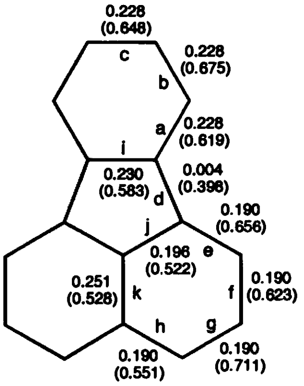

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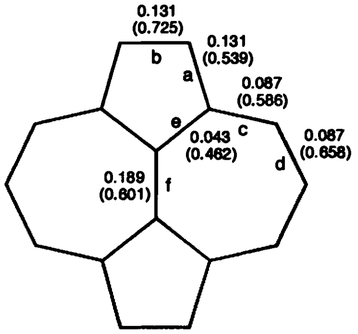

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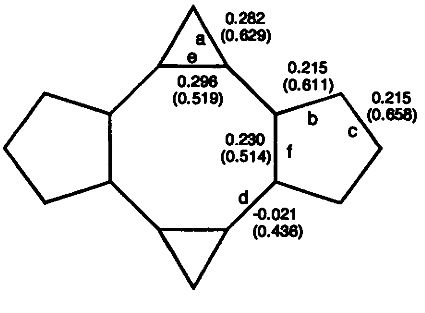

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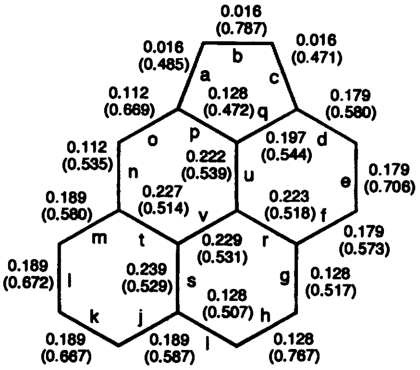

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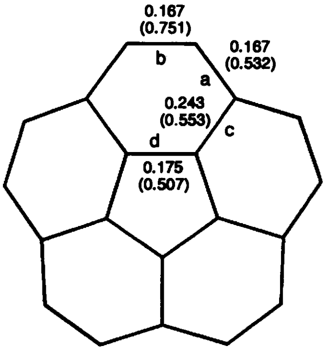

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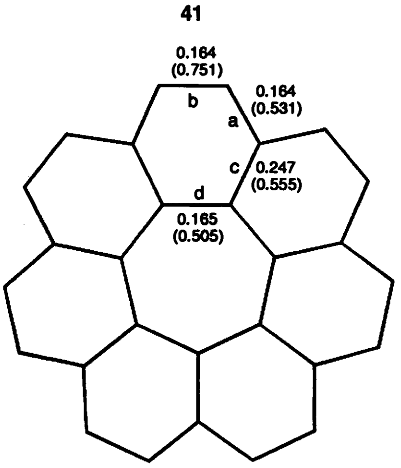

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Table 2 Topological and percentage resonance energies for polycyclic non-benzenoid hydrocarbons

Species	$E_{tr}/\lvert\beta\rvert$	$\%E_{tr}$
Cyclobutadiene (**18**)	−1.226	−23.46
Cyclooctatetraene (**19**)	−0.595	−5.80
Butalene (**20**)	−0.604	−7.31
Pentalene (**21**)	−0.215	−2.02
Benzocyclobutene (**22**)	−0.393	−3.65
Azulene (**23**)	0.151	1.14
Bicyclo[6.2.0]decapentaene (**24**)	−0.461	−3.46
Heptalene (**25**)	−0.141	−0.89
Triafulvalene (**26**)	−0.461	−5.81
Calicene (**27**)	0.433	4.13
Fulvalene (**28**)	−0.299	−2.28
Sesquifulvalene (**29**)	0.272	1.73
Heptafulvalene (**30**)	−0.218	−1.20
Biphenylene (**31**)	0.123	0.75
s-Indacene (**32**)	0.055	0.34
as-Indacene (**33**)	−0.306	−1.89
Acenaphthylene (**34**)	0.354	2.18
Cyclopent[*cd*]azulene (**35**)	0.101	0.62
Aceheptylene (**36**)	0.105	0.56
Pyracylene (**37**)	0.106	0.55
Fluoranthene (**38**)	0.578	2.64
Azupyrene (**39**)	0.217	0.99
Cyclic bicalicene (**40**)	0.657	2.97
Cyclopenta[*cd*]pyrene (**41**)	0.565	2.27
Corannulene (**42**)	0.735	2.63
[7]Circulene (**43**)	1.011	2.58

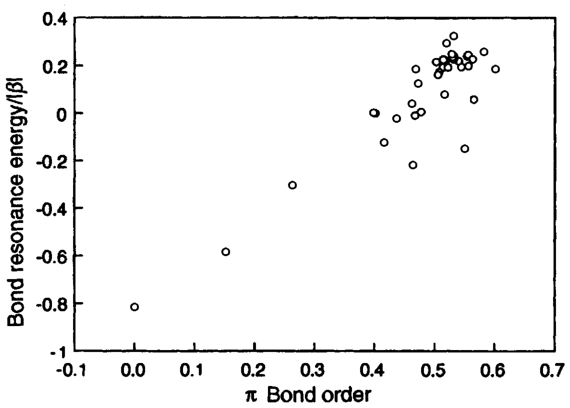

Fig. 5 Bond resonance energies *versus* π bond orders for non-benzenoid hydrocarbons

Bond resonance energies for cyclobutadiene (**18**), butalene (**20**), benzocyclobutene (**22**), bicyclo[6.2.0]decapentaene (**24**) and biphenylene (**31**) indicate that the cyclobutadiene ring markedly destabilizes the conjugated system. This confirms the idea that a four-membered conjugated circuit is highly anti-aromatic in nature.[19,21] As can be seen from the bond resonance energies of cyclooctatetraene (**19**), pentalene (**21**), **22** and **24**, eight-membered conjugated circuits are also a destabilizing factor.

It has been reported that **21** is not only highly anti-aromatic but also highly reactive with a large negative percentage resonance energy.[13,23] This molecule may be viewed as perturbed cyclooctatetraene because of the fact that bond c is an essential single bond and does not create additional conjugated circuits.[19,21] However, this interpretation is not consistent with their bond resonance energies. Planar cyclooctatetraene (**19**) is highly anti-aromatic with a percentage resonance energy of −5.80.[13,23] Bonds a and b in **21** really have large negative bond resonance energies, whereas bond c has a large positive one. This indicates that the peripheral eight-membered conjugated circuit dominates the anti-aromatic character of this molecule, but that the cross-link is very effective in diminishing the degree of anti-aromaticity due to the peripheral circuit even if the π-order is very small. It is obvious that Platt's perimeter model[30,31] cannot be applied to **21**.

In many other polycyclic non-benzenoid systems, π bonds shared by odd-membered rings are never small perturbations. These bonds tend to diminish the degree of aromaticity or anti-aromaticity due to adjacent conjugated circuits. Bond d in heptalene (**25**) and bond d in *s*-indacene (**32**) are such examples. A reason why bond resonance energies of bond g in **35** and bond i in **36** are large may likewise be that they are located inside the local pentalene and heptalene structures, respectively. *as*-Indacene (**33**) is much less aromatic than **32** since the former species can be regarded as a substituted fulvalene. Fulvalene (**28**) is anti-aromatic with a percentage resonance energy of −2.28. Therefore, even if bond e or f in **33** is made olefinic artificially, the entire conjugated system remains anti-aromatic with a topological resonance energy of −0.18 $|\beta|$.[13,23]

Azulene (**23**) deserves special attention because it is the best known non-benzenoid hydrocarbon with a moderately large percentage resonance energy and undergoes various electrophilic substitution reactions.[13,23,37] This molecule can be viewed exceptionally as perturbed [10]annulene since cross-link f, which is a formal single bond, has a negligibly small bond resonance energy. If [10]annulene is made planar, it must be moderately aromatic with a percentage resonance energy of 1.25, which is comparable in magnitude to that of 1.14 for **23**.[13,23] It is interesting to see that **23** alone conforms to Platt's perimeter model[30,31] as cross-link f can really be regarded as a small perturbation.

Fulvalenes **26**–**30** are noteworthy in that their aromatic character cannot be explained in terms of the original conjugated-circuit theory.[18–22] For example, **27** is aromatic although there are no aromatic conjugated circuits in it. Calculated bond resonance energies revealed that the two rings contribute much to the aromaticity, suggesting that the trigonal and pentagonal rings are charged and behave as if they were aromatic cyclopropenium- and cyclopentadienide-like ions, respectively. As a result, all π bonds located along these two rings have large positive bond resonance energies. It then follows that the π bond order of bond f, which links the two rings, is very small for a formal double bond. Pentagonal and heptagonal rings in sesquifulvalene (**29**) likewise seem to be charged to form aromatic cyclopentadienide- and tropylium-like ions, respectively. All symmetric fulvalenes have negative topological resonance energies, so all the π bonds located along the rings have negative bond resonance energies.

Essentially the same situation is encountered when discussing the aromatic character of **40**.[38,39] This molecule formally consists of two calicene units connected by two C–C bonds. These C–C bonds are not essential single bonds, but parts of the 16-membered conjugated circuit, the only conjugated circuit in **40**. This conjugated circuit is anti-aromatic in nature. However, bond d and the equivalents located along the circuit contribute little to anti-aromaticity. Instead, bonds e and f contribute much to the aromaticity although they are nothing other than formal single bonds. Calculated bond resonance energies suggest that, as in the case of **27**, two three- and two five-membered rings in **40** are highly aromatized by bearing positive and negative charges, respectively. As pointed out previously,[39–41] kekulene (**17**) and **40** are not superaromatic at all, in the sense that no extra stabilization energy due to the super-ring structure can be expected.

The original conjugated-circuit theory has been parametrized in such a manner that it reproduces well the Dewar resonance energies of polycyclic benzenoid hydrocarbons.[18–21] As mentioned above, this theory cannot be used to justify the topological resonance energies of **26**–**30** and **40**. Dewar resonance energies of **27** and **40** (C_{2h}) were calculated to be 4.5 and 16.5 kcal mol^{-1},† respectively, indicating that they are moderately aromatic even in the SCF-MO level.[39] Note that the Dewar resonance energy of **1** is 20.0 kcal mol^{-1}.[6] Positive Dewar

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† 1 cal = 4.184 J.

resonance energy values for **27** and **40** cannot be reproduced by the conjugated-circuit theory, simply because there are no aromatic conjugated circuits in these molecules. Herndon and Ellzey noted that zwitterionic structures may contribute much to the aromaticity of such compounds,[19] but that it is not taken into account in the theory. It is desirable to improve the conjugated-circuit theory by taking account of zwitterionic structures or by defining charged odd-membered conjugated circuits.[42]

In conjunction with his argument for the perimeter model, Platt proposed that non-benzenoid hydrocarbons such as pyranene (**44**), coranene (**45**) and ovanene (**46**) might possibly be stable because they have a continuous perimeter of $4n + 2$ carbon atoms.[30] These hypothetical molecules have a $(4n + 2)$-membered conjugated circuit along the periphery. Conjugated systems of these three hydrocarbons are shown in Fig. 6. Their topological and percentage resonance energies are listed in Table 3. We found that, contrary to the prediction based on the perimeter model, **44** is anti-aromatic whereas **45** and **46** are essentially non-aromatic. Since none of them are predicted to be aromatic, it is clear that the perimeter model does not hold for these Platt hydrocarbons. As peripheral conjugated circuits in these molecules are very large, they never contribute much to aromaticity. Most of the peripheral C–C bonds in **44**–**46** have negative bond resonance energies.

Molecular ions of non-benzenoid hydrocarbons

There is no doubt that benzenoid hydrocarbons whose carbon skeletons represent graphitic fragments have high thermodynamic stability. Therefore, one might presume that a charged non-benzenoid hydrocarbon must be highly stable if it is iso-π-electronic with an appropriate benzenoid hydrocarbon (Table 4).[42,43] The bond resonance energies and the π bond orders for five charged non-benzenoid hydrocarbons are compared in Fig. 7. These molecular ions are iso-π-electronic with some neutral benzenoid hydrocarbons, and are really highly aromatic with large positive percentage resonance energies. The pentalene molecular dianion (21^{2-}) and the heptalene molecular dication (25^{2+}) are iso-π-electronic with **2**. Molecular dianions of *s*-indacene (32^{2-}) and *as*-indacene (33^{2-}) are iso-π-electronic with **3** and **4**, respectively. The pyracylene dianion (37^{2-}) is iso-π-electronic with **8**. All these molecular ions have so far been prepared.[37]

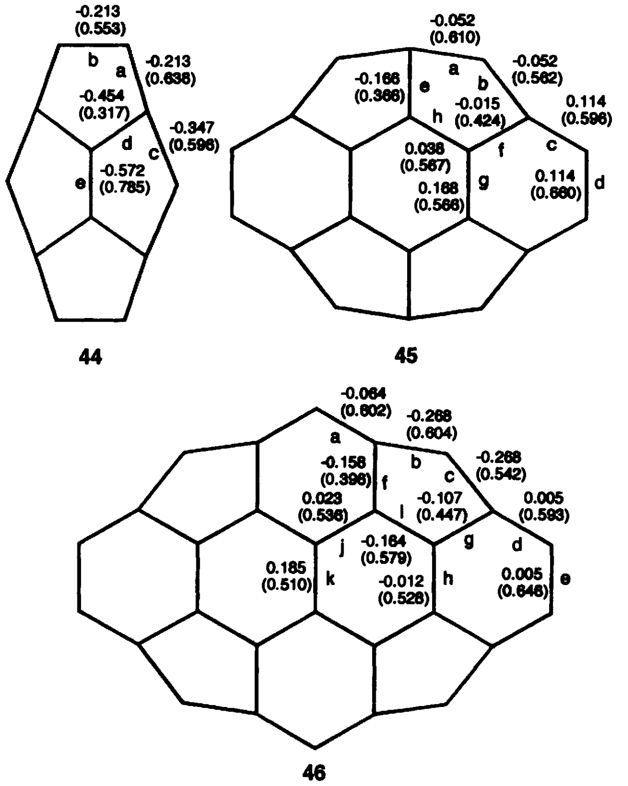

Fig. 6 Bond resonance energies for Platt hydrocarbons. Values in parentheses are π bond orders.

Table 3 Topological and percentage resonance energies for Platt hydrocarbons

Species	$E_{tr}/\lvert\beta\rvert$	$\%E_{tr}$
Pyranene (**44**)	−0.548	−3.27
Coranene (**45**)	0.064	0.23
Ovanene (**46**)	0.141	0.35

As in the case of neutral benzenoid hydrocarbons, all π bonds shared by two rings in these molecular ions are more aromatic than peripheral ones. This indicates that all the rings behave as a kind of aromatic conjugated circuit even if they are odd-membered ones. The presence of bond h in **33** and bond e in **37** obviously enhances the degree of aromaticity in the corresponding molecular ions. Bond c in 21^{2-}, bond d in 25^{2+}, bond d in 32^{2-} and bond f in 37^{2-} have the same large positive bond resonance energies as the corresponding bonds in the

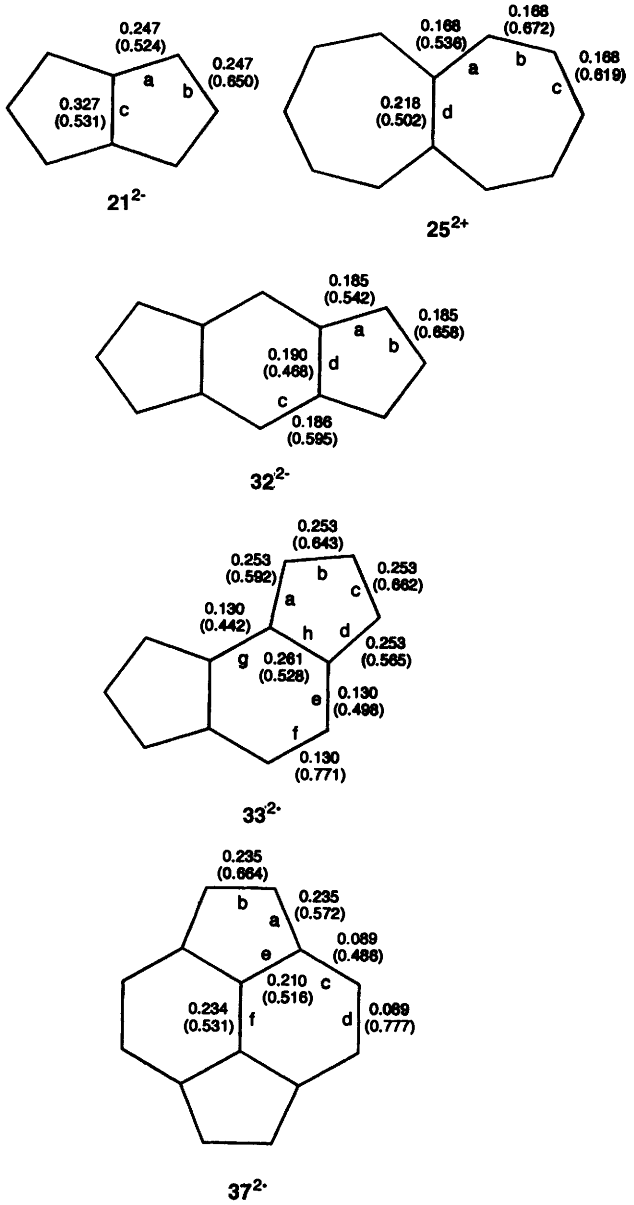

Fig. 7 Bond resonance energies for charged non-benzenoid hydrocarbons. Values in parentheses are π bond orders.

Table 4 Topological and percentage resonance energies for charged non-benzenoid hydrocarbons

Species	$E_{tr}/\lvert\beta\rvert$	$\%E_{tr}$
Pentalene dianion (**21**$^{2-}$)	0.464	4.64
Heptalene dication (**25**$^{2+}$)	0.314	2.05
s-Indacene dianion (**32**$^{2-}$)	0.475	3.01
as-Indacene dianion (**33**$^{2-}$)	0.574	3.63
Pyracylene dianion (**37**$^{2-}$)	0.539	2.86

neutral species. The role of the first three bonds in the ionized state, however, is quite different from that in the neutral state. In the neutral state, these bonds relax the anti-aromaticity induced by the peripheral conjugated circuit. In the ionized state, these bonds are strengthened by the aromatization of the rings sharing them.

In this context, **21**, **32** and **37** are all characterized by the lowest unoccupied molecular orbital (LUMO) which is non-bonding in nature. These molecules gain no additional π binding energy even if they acquire two more π electrons to form molecular dianions. π Bond orders of all C–C bonds remain unchanged, but the topological resonance energy and all the bond resonance energies increase to a considerable extent (Table 4). This simply reflects the fact that the total π binding energy of a polyene reference always decreases by forming a molecular ion. Then, **21**$^{2-}$, **32**$^{2-}$ and **37**$^{2-}$ can be considered to be thermodynamically stable for such molecular dianions. On the other hand, the highest occupied molecular orbital (HOMO) of **25** is non-bonding in nature. For basically the same reason, **25**$^{2+}$ is very stable for a molecular dication.

Bond resonance energy and chemical reactivity

In general, a highly aromatic molecule is kinetically stable. However, the isolability of a molecule does not always correlate with the percentage resonance energy. This is to be expected because even an aromatic molecule may have a reactive substructure that can be transformed into a kinetically more stable system.[23] We previously evaluated two typical reactivity indices, localization energy[44,45] and superdelocalizability,[46,47] for all sites in various non-benzenoid hydrocarbons, and clarified that the majority of non-benzenoid hydrocarbons are chemically reactive even if they are sufficiently aromatic with positive percentage resonance energies.[48,49] They have sites that are very susceptible to electrophilic and/or nucleophilic addition and/or substitution. The present bond resonance energy method enables one to obtain a clue to the degree of chemical reactivity or kinetic instability without referring to particular chemical reactions.

In a previous paper,[23] we analysed the bond resonance energies for a series of fullerenes in detail. The 5/5 bonds in fullerenes with abutting pentagons are in marked contrast to those in **21** and **35**, in that the former bonds are highly anti-aromatic with large negative bond resonance energies. This was taken as the primary reason why fullerenes with abutting pentagons cannot be isolated.[26,27] The success of the bond resonance energy model in verifying the IPR is owed presumably to the fact that fullerene conjugated systems consist of rather uniform type-I C–C bonds only. The 5/5 bonds in fullerene molecule, if any, are shared by many anti-aromatic conjugated circuits, whereas the 5/5 bonds in planar hydrocarbons **21** and **35** are not shared by any anti-aromatic conjugated circuits, so are never anti-aromatic. Thus, it is interesting to note that 5/5 bonds in non-IPR fullerenes greatly destabilize the conjugated subsystem, but that 5/5 bonds in **21** and **35** are a stabilizing factor.

Planar benzenoid and non-benzenoid hydrocarbons have not only type-I but also type-II C–C bonds. It is not easy to predict from the bond resonance energies the sites of high reactivity. This is because a chemical reaction often changes the nature of the conjugated system to a great extent. For example, one may expect that **4** is reactive around the central ring since four of the constituent bonds have relatively small bond resonance energies. As is known, addition occurs at bond g but not at bond f with the same bond resonance energy so as to retain the highest degree of aromaticity.[28] If it occurs at bond f with the same bond resonance energy, all residual π bonds become fixed single or double bonds.

Only when there are fixed or essential double bonds in a molecule, can one safely predict that they are very or fairly reactive with very small bond resonance energies. For example, double bonds fixed in the central rings of **12** are very reactive. This hydrocarbon reacts with maleic anhydride immediately at room temperature.[28] Fixed double bonds in semi-benzenoid hydrocarbons, such as **34** and **41**, are also olefinic with very small bond resonance energies, so must be chemically as reactive as linear polyenes.[50,51] In general, double bonds fixed in Kekulé or Clar structures presumably tend to undergo 1,2-addition-type reactions. In contrast, single bonds fixed in Kekulé or Clar structures are not reactive even if they have small bond resonance energies. In the case of C_{60} (I_h), 5/6 bonds with smaller bond resonance energies are susceptible to insertion reactions.[52,53]

Many of the non-benzenoid hydrocarbons have one or more π bonds with very small or negative bond resonance energies. Even in such a case, chemical reactions cannot be expected to occur just at these bonds. It, however, is true that π bonds with negative bond resonance energies are the origin of not only thermodynamic, but also kinetic instability. What we can safely say about all cyclic conjugated systems is that a molecule must be kinetically unstable or chemically reactive if it has one or more π bonds with large negative bond resonance energies. A molecule with such anti-aromatic local structures will tend to transform into some kinetically more stable species. Many non-benzenoid hydrocarbons are unstable in this sense. A polyacene molecule becomes more reactive on going to a higher member as the bond resonance energies of all the peripheral C–C bonds become smaller.[28,29]

Conclusions

The bond resonance energy concept may be traced back to the work carried out in 1978 by Gutman *et al.*[54] They showed that the topological resonance energy can be partitioned exactly among the constituent π bonds in the conjugated system. The present definition of the bond resonance energy is better suited at least for discussing in detail the effect of individual conjugated and non-conjugated circuits on aromaticity and chemical reactivity. Our bond resonance energy method is very easy to handle. No parametrization is involved in our theoretical framework. The bond resonance energies can easily be calculated for any very large conjugated system even if the topological resonance energy cannot be calculated for it.

As has been described above, the bond resonance energy method can be used to analyse the geometric origin of aromaticity in a polycyclic conjugated system. It can readily be applied not only to neutral but also to charged species, and allows one to predict the degree of kinetic stability or instability without referring to particular chemical reactivities. The negative sign of the bond resonance energy is a simple but straight forward indication of kinetic instability. Calculated bond resonance energies also proved to be useful for exploring the utility and the limitations of the conjugated-circuit theory[18–22] and Clar's intuitive structural formulae.[28,29] Platt's perimeter model[30,31] was disproved simply by inspecting the bond resonance energies of the peripheral C–C bonds.

We have in this paper assumed that all C–C bond lengths are equal for all conjugated hydrocarbons investigated. In fact, highly anti-aromatic conjugated systems are expected to appear in a less symmetric geometry.[55] Many anti-aromatic and olefinic non-alternant systems are considerably stabilized by introducing marked bond-length alternation into anti-aromatic or olefinic substructures. Unstable alternant hydrocarbons are not exceptions. For example, **31** is fairly stable although two of the π bonds around the four-membered ring have very large negative bond resonance energies.[56] In the actual biphenylene molecule, the anti-aromaticity due to these π bonds are relaxed by the unusual elongation of two of them.[56] Thus, the bond resonance energies will help us understand how and why a pattern of bond distortions is formed in polycyclic conjugated systems.

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