

Aromaticity Today: Energetic and Structural Criteria

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Abstract

Aromaticity appears to be among the most controversial concepts in modern chemistry. The present paper addresses current controversies in development and applications of the two main criteria of aromaticity, namely, energetic and structural criteria. Various types of resonance energy with an emphasis on homodesmotic and isodesmic stabilization energies have been discussed. Reliability of such structural criteria of aromaticity as equalization of carbon-carbon bond lengths and stability with respect to out-of-plane distortions of a molecular structure has been analyzed using various examples.

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Aromaticity appears to be among the most controversial concepts in modern chemistry (1–9). The problems in determining the effects caused by aromaticity or antiaromaticity result from the inability to measure these effects *directly* by any physical or chemical experiment. Of course, in this respect, aromaticity and antiaromaticity are perfectly analogous to many other theoretical concepts such as, for example, strain energy or the charge on an atom in a molecule.

It is no wonder that a debate has been going on for a considerable time as to whether the term “aromaticity” may be regarded as scientifically legitimate (10, 11). Nevertheless, the concept of aromaticity plays such an important role in teaching organic chemistry and in conducting research that proposals to do away with it are not realistic. Rather than discard the concept, there is a need for additional analysis leading to a deeper understanding of “aromaticity”. However, the multifaceted nature of the aromaticity concept makes it unreasonable to aim any paper, including the present one, at yielding a simple succinct answer to the question of what aromaticity is and what the criteria for aromaticity are. Still, I hope that a discussion of key criteria of aromaticity such as molecular energetics and structures can save students from trepidation upon being asked to define the term “aromaticity”.

What Criteria of Aromaticity Do We Need?

Various criteria for aromaticity are known (1–8). However, since it is impossible to define aromaticity exhaustively, there is no unambiguous yardstick for assigning a compound to the aromatic or antiaromatic class. The most important requirements that a criterion of aromaticity should meet are as follows: (i) it must be directly related to some known physical or chemical effect regarded as a manifestation of aromaticity and this effect must be experimentally quantifiable; and (ii) it is essential that the fulfillment of the chosen criterion should indicate the presence of such properties in a given compound as are commonly regarded to be the main attributes of aromaticity.

The main criteria of aromaticity are energetic, structural, and magnetic ones. In some cases, not all of the main criteria of aromaticity are satisfied concurrently (1). This discordance can be accounted for by the fact that the criteria may refer to different, mutually “orthogonal” groups (12–14). The present paper addresses current controversies in development and applications of energetic and structural criteria. A detailed consideration of the current status of magnetic criteria can be found elsewhere (1, 15–22).

Energetic Criteria

Various Types of Resonance Energy

To a chemist, the aromaticity or antiaromaticity of a compound is primarily associated with its stability or

instability with respect to valence isomerizations, intra- and intermolecular cyclizations, recyclization reactions, etc. (1–8). The reactivity of aromatic compounds is characterized by a so-called regeneration, “the tendency to retain the type” (23). The original type of the electronic system, lost at a certain reaction stage, is restored in the products (24). Such regenerative (or “meneidic” [23]) behavior of aromatic compounds is regarded as a manifestation of their special stability. All this was apparently a good reason for assigning the dominant role in determining the aromaticity and, later, antiaromaticity to the energy criterion that rests on energy estimates of aromatic stabilization (or antiaromatic destabilization).

Aromaticity is manifested in the nonadditivity of the collective, primary energetic, properties of a molecule. This nonadditivity is assigned to the effect of the “cyclic electron [bond] delocalization” (25), in contrast to the model of bond localization that breaks down for aromatic or antiaromatic molecules. However, the stability of a compound characterized by cyclic electron delocalization may depend on other factors in addition to aromaticity. Therefore, in order to classify a compound as aromatic, antiaromatic, or nonaromatic, it is necessary to separate the stabilization or destabilization caused by the cyclic electron delocalization from the net stabilization (1). To determine this contribution, quantum chemical and experimental schemes have been devised for estimating the resonance energy (RE) or stabilization energy (SE). From the viewpoint of the formalism used to calculate resonance energies, various schemes of calculating REs and SEs that serve as quantitative indexes of the aromaticity (antiaromaticity) (1, 26–44) formally fall into two groups. In one of these, *numerical values* of REs are derived from either experimental thermochemical data or, if these are not available, quantum chemical calculations. The latter are based on a variety of approaches from the Hückel MO theory (the RE scheme developed by Hess and Schaad [30, 31]) and PPP methods (28, 29) to *ab initio* calculations in which MO or VB theory is employed (15, 16, 32, 35, 44–54). Another group comprises graph-theoretical and combinatorial methods for obtaining *analytical expressions* for REs (21, 36–41). The schemes of the first category give fairly exact values. The latter, though not so accurate because they are confined mainly in the framework of the Hückel theory, reveal trends in the evolution of REs and thus of the aromaticity (antiaromaticity) for a broad spectrum of compounds.

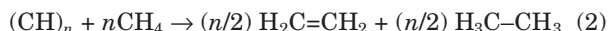
There are two intrinsically different types of resonance energy. The first is represented by various schemes of resonance energy, which are invoked to evaluate effects of *net* (cyclic and noncyclic) π -electron delocalization or effects associated only with π -electron noncyclic delocalization. For estimating the net delocalization effect, the reference structure must have “isolated” (non-interacting) double bonds (35). The second type of resonance energies is used to calculate aromatic (antiaromatic) stabilization (destabilization) and refers to the part of the total energy that reflects the π -electron *cyclic* (bond) delocalization (25). The procedure to calculate this kind of resonance energy and, therefore, to evaluate aromatic (antiaromatic) effects should be based

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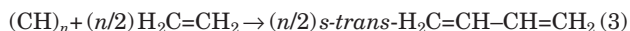
on a model reference structure whose energy would differ from that of the cyclic structure by precisely the component corresponding to the cyclic delocalization (1). Both types of resonance energies (also called stabilization energies for π -conjugation systems) characterize the nonadditivity effects caused by cyclic and noncyclic π -electron delocalization. The stabilization energy of a molecule can be calculated as the difference between the heat of atomization, ΔH_a , or heat of formation, ΔH_f , of a given molecule and the same energetic parameter obtained using an additivity scheme (34). For example, for [n]annulene we have

$$SE = \Delta H_a(C_nH_n) - nE(C-H) - (n/2)E(C-C) - (n/2)E(C=C) \quad (1)$$

The difference between the two types of stabilization energies lies in the type of the reference structure, whose energy is found by an additivity scheme. As seen from eq 1, the specificity of each scheme for calculating resonance energy depends on the procedure employed to calculate the bond energies $E(C-H)$, $E(C-C)$ and $E(C=C)$. The reference system having noninteracting (ethylene-type) double bonds serves for estimating the net stabilization, and therefore, CH_4 , H_3C-CH_3 , and $H_2C=CH_2$ are taken as the reference molecules to calculate the bond energies. In this case eq 1 leads to an estimation of the energy of reaction 2, which is the *isodesmic stabilization energy* (ISE) (55). This energy corresponds to the net stabilization of [n]annulene due to π -electron delocalization and can be traced back to the Hückel resonance energy (1).



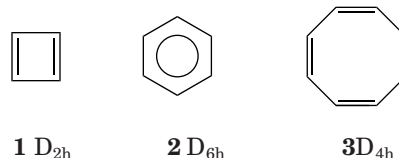
If the bond energies determined from the additive energies of acyclic polyenes having equilibrium geometry as suggested by Dewar (28) are used to calculate energy of hypothetical reference structure, eq 1 transforms into the homodesmotic reaction eq 3 for estimating aromatic stabilization energy of [n]annulene (33). Therefore, if the bond energies in eq 1 are calculated from the ΔH_a values taken for the set of the reference molecules (such as $H_2C=CH_2$ [to model the isolated double C=C bond] and *s-trans*-1,3-butadiene [to model the single =C-C= bond and the conjugated C=C- bond]), the energy due to the aromatic stabilization or antiaromatic destabilization of [n]annulene (33, 34) can be obtained from the enthalpy of reaction (3). This *homodesmotic stabilization energy* (HSE) corresponds to the stabilization caused by the π -electron *cyclic* delocalization (25) and can be interpreted as analogous to the Dewar resonance energy (1).



Homodesmotic and Isodesmic Stabilization Energies and Their Relevance to Absolute Antiaromaticity

The scheme of the homodesmotic stabilization energies (HSE) (33) has been used increasingly in recent years (5, 34, 47–54). Apparently, it has become the most dependable tool for obtaining numerical estimates of aromatic stabilization or antiaromatic destabilization. This is partly explained by the growing amount and increasing accuracy of experimental thermodynamic data on organic compounds (56, 57). A still more important reason is the rapid development of *ab initio* computational methods (55) that enable the HSE to be calculated even when some experimental data are lacking or if a compound under question is experimentally unknown.

The HSE values for cyclobutadiene **1**, benzene **2**, and the planar D_{4h} structure of cyclooctatetraene **3** are listed in Table 1. The calculated value for benzene agrees very well with the experimental HSE value. The antiaromatic destabilization of cyclobutadiene, which is corrected for the ring-strain and normalized per π -electron ($-41.55 \text{ kJ mol}^{-1}$), is larger (in absolute value) than the antiaromatic destabilization of the planar D_{4h} cyclooctatetraene ($-14.85 \text{ kJ mol}^{-1}$ per π -electron) and the aromatic stabilization of benzene ($15.53 \text{ kJ mol}^{-1}$ per π -electron) (Table 1). Cyclobutadiene is remarkably unstable (58) and its antiaromaticity is the driving force of this instability. An antiaromatic molecule having both a negative HSE value and a negative ISE value (i.e., the molecule has net destabilization) can be classified as *absolute* antiaromatic. In other words, such a molecule is antiaromatic regardless of what reference model is used (59, 60).



[n]Annulenes are assigned to antiaromatic systems if their homodesmotic stabilization energies are negative. However, this does not imply explicitly that antiaromatic species must possess net destabilization. The isodesmic bond-separation reactions (55) yield net stabilization (destabilization) energy and therefore cannot be used for estimating either aromatic stabilization or antiaromatic destabilization (1). It is easy to see from eqs 2 and 3 that the ISE and HSE values for [n]annulene differ from each other by the $(n/2)$ ISE(*s-trans*-1,3-butadiene) value calculated using eq 4. As the ISE(*s-trans*-1,3-butadiene) is positive (its experimental value calculated from the heats of formation [56, 57] is 59.4 ± 4.1

Table 1. Isodesmic and Homodesmotic Stabilization Energies (ISE and HSE) of Cyclobutadiene (D_{2h}), Benzene, and Cyclooctatetraene (D_{4h}) (in kJ mol^{-1})^a

Molecule	ISE	ISE per π electron	HSE	HSE per π electron
Cyclobutadiene 1 , D_{2h}	-43.8 ^b	-10.95	-166.2 ^c	-41.55
Benzene 2 , D_{6h}	276.8 ^d	46.13	93.2 ^e	15.53
Cyclooctatetraene 3 , D_{4h}	118.8	14.85	-118.8	-14.85

^aStabilization energies for cyclobutadiene and benzene were calculated using G2 theory (53, 54). The ISE and HSE values for the planar D_{4h} cyclooctatetraene were computed at the MP4SDTQ/6-31G(d,p)//MP2/6-31G(d,p) + ZPE(HF/6-31G(d)) level.

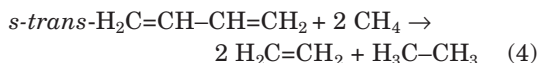
^b-184.4 kJ mol^{-1} without the correction for strain energy. The strain energy of cyclobutadiene estimated from the experimental strain energies of cyclobutane and cyclobutene is $140.6 \text{ kJ mol}^{-1}$ (54).

^cThe HSE (**1**) calculated without the correction for strain energy is $-306.8 \text{ kJ mol}^{-1}$. The HSE value relates to the ISE value by means of eq 5. G2 theory yields the ISE of *s-trans*-1,3-butadiene to be 61.2 and 58.9 kJ mol^{-1} at 0 and 298 K, respectively (53). This agrees well with the experimental ISE value of $59.4 \pm 4.1 \text{ kJ mol}^{-1}$ at 298 K. Calculations at the MP4SDTQ/6-31G(d,p)//MP2/6-31G(d,p) + ZPE(HF/6-31G(d)) level give the ISE(*s-trans*-1,3-butadiene) value of 59.4 kJ mol^{-1} (at 0 K).

^dThe ISE (**2**) calculated using G2 theory is $269.1 \text{ kJ mol}^{-1}$ at 298 K (53). The experimental ISE value for benzene **2**, calculated from the experimental heats of formation (56), is $268.7 \pm 6.3 \text{ kJ mol}^{-1}$ at 298 K.

^eThe HSE(**2**) calculated using G2 theory is 92.5 kJ mol^{-1} at 298 K (53). The experimental HSE value calculated from the experimental heats of formation (56, 57) is $90.5 \pm 7.2 \text{ kJ mol}^{-1}$ at 298 K.

kJ mol^{-1} at 298 K), the ISE value for [n]annulenes is always larger than the HSE value (see eq 5). This reflects the stabilization of the conjugated systems of [n]annulenes, which is caused by π -electron delocalization (44, 46, 61, 62).



$$\text{ISE}(\text{C}_n\text{H}_n) = \text{HSE}(\text{C}_n\text{H}_n) + (n/2) \text{ISE}(s\text{-trans-1,3-butadiene}) \quad (5)$$

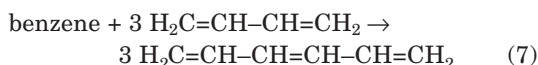
The net destabilization means that not only is the $\text{HSE}(\text{C}_n\text{H}_n)$ value negative but the isodesmic stabilization energy is negative as well ($\text{ISE}[\text{C}_n\text{H}_n] < 0$). It takes place if $\text{HSE}(\text{C}_n\text{H}_n) < 0$ and inequality 6 is fulfilled:

$$-\text{HSE}(\text{C}_n\text{H}_n) > (n/2) \text{ISE}(s\text{-trans-1,3-butadiene}) \quad (6)$$

In other words, if [n]annulene is absolute antiaromatic, its antiaromatic destabilization should be larger (in absolute value) than the $(n/2)$ $\text{ISE}(s\text{-trans-1,3-butadiene})$ value. While the planar cyclooctatetraene **3** has only the relative antiaromatic character (the $\text{ISE}[\mathbf{3}]$ value is positive), cyclobutadiene features both *relative* and *absolute* antiaromaticity. The isodesmic stabilization energy of cyclobutadiene, corrected for the strain energy is still negative ($-43.8 \text{ kJ mol}^{-1}$; Table 1) because of the large (in absolute value) antiaromatic destabilization of cyclobutadiene. (The HSE value is $-166.2 \text{ kJ mol}^{-1}$; Table 1.) This conclusion agrees with the analysis of the π -electron localization in [n]annulenes **1–3** using π -type localized MOs (60).

For polycyclic molecules, the homodesmotic reactions to estimate aromaticity are not always uniquely determined. Several schemes of homodesmotic reactions may be conceivable for the same polycyclic molecule (33).

The scheme of the hyperhomodesmotic reactions (32) takes into account the distinctions between various kinds of bonds in a more subtle way than the HSE scheme does. Indeed, the three $\text{H}_2\text{C=CH}_2$ and three HC=CH bonds on the left side of eq 3 are replaced by the HC=CH_2 bond on the right. This incongruity can be avoided (eq 7) (32):



At the MP4SDTQ/6-31G(d,p)//MP2(full)/6-31G(d,p) level, the hyperhomodesmotic stabilization energy of benzene is 84.9 kJ mol^{-1} (51).

Other Approaches for Calculating Resonance Energies

Besides the RE calculations, schemes based on general theoretical models that also rest on the energy criterion, but of a more specific character, may be applied. These models include various other quantitative characteristics of chemical reactions, such as the breaking up or formation of an aromatic (antiaromatic) system (see, e.g., refs 1, 3, 5, 8). Calculations of the empirical resonance energies derived from enthalpies of combustion or hydrogenation reactions produce a considerable scatter in RE values. The empirical resonance energies are not discussed here. Interested readers can find their critical analysis in the review (63) and in books (1, 2).

Interrelation between Energetic Criteria and Other Criteria of Aromaticity

Is the interrelation among criteria of aromaticity always clear-cut? Will the aromaticity inferred from an energetic criterion be confirmed, say, by magnetic crite-

ria? The model underlying all schemes of the magnetic criteria is the ring-current model (64, 65). A number of quantitative relationships have been established between RE values and aromaticity indexes based on this model. We can see now the growing interest in the magnetic criterion rested on the exaltations of magnetic susceptibilities as indexes of aromaticity (15–18). The calculations of these exaltations using the IGLO method (66) have opened the possibility not only to evaluate the aromaticity of unstable molecules for which the experimental measurement of magnetic exaltations is difficult (15, 16), but also to estimate the aromatic or antiaromatic character of the transition structures for pericyclic reactions (17). There are some cases of the interrelation between REs and magnetic susceptibilities (15, 21, 67, 68), although the proportionality of these two quantities may not always be observed for polycyclic molecules (21, 68). The parallelism is also lost in large [4n]annulenes (69). There is a direct relationship between the energy criteria of aromaticity and electron count rules, such as the $4n + 2$ Hückel rule (70), which represent a convenient tool for qualitative verification of aromaticity of a given compound (see, e.g., refs 1, 2).

Structural Criteria

Viewed from the energetic criterion of aromaticity, structural criteria must reflect those features in the molecular geometry that lead to stabilization of a cyclic conjugated system. Historically, formulation of the structural criteria has rested on the idea that cyclic π -electron delocalization causes the aromatic stabilization. The following manifestations of the π -delocalization are considered in this connection: the planar geometry of the ring as caused by the requirement for a better overlap of the p_π -orbitals, and equalization of the carbon–carbon bond lengths in the ring (1–5). The latter implies that a high symmetry structure of a given molecule is a minimum on the potential energy surface (PES). In the most concentrated form these attributes are present in the benzene molecule. Therefore, structural criteria should be functions that determine to what extent these attributes are close to the ones for benzene.

As the structural indexes constructed in this fashion are phenomenological, one is entitled to ask whether the specific features in the geometry of the aromatic and antiaromatic molecules used to work out such indices are indeed determined, and if so, to what degree, by the π -electron cyclic (bond) delocalization.

Equalization of Carbon–Carbon Bond Lengths as a Feature of Aromatic Molecules Contrasted to Bond-Length Alternation in Antiaromatic Molecules

Aromatic and antiaromatic molecules and acyclic polyenes have dissimilar geometries, differing primarily in bond lengths. These differences are a basis for the structural indexes of aromaticity reflecting the degree of alternation of the CC bond lengths in a ring. According to experimental data (1, 3–5), the benzene molecule has a structure of D_{6h} symmetry with equal CC bond lengths (1.3902 \AA [71]). In contrast to benzene, acyclic polyenes are characterized by alternation of bond lengths. The lengths of the CC bonds in benzene are intermediate between the C–C and C=C bond lengths in acyclic polyenes (e.g., 1,3-butadiene and 1,3,5-hexatriene) (1). For antiaromatic molecules, the bond-length alternation is even more pronounced than for acyclic polyenes (1). For instance, the D_{2h} structure of cyclobutadiene **1** has C=C and C–C bond lengths of 1.3435 and 1.5639

Å, respectively, calculated at the MP2/6-31G(d,p) level (1). Unlike aromatic molecules, as a rule, a high-symmetry structure of the lowest singlet state of an antiaromatic molecule does not correspond to a minimum on the PES (72–74). For example, the $^1B_{1g}$ state structure of cyclobutadiene with equal CC bond lengths corresponds to a transition structure for the topomerization of the rectangular D_{2h} structure **1** with a barrier of 26.8 kJ mol $^{-1}$ (74).

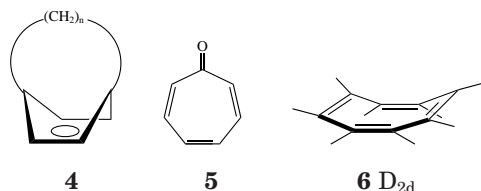
The structural criterion of aromaticity, based on the requirement for equality of the carbon–carbon bond lengths, has been recently subjected to severe tests. Does the D_{6h} structure of benzene originate from its aromatic π -system or does benzene owe its structure to the σ -system? This is the subject of intensive debate (42, 46, 61, 62, 75–77). An important point is that if the π -system of benzene favors a D_{3h} geometry, the aromatic stabilization caused by π -electron delocalization decreases upon the $D_{6h} \rightarrow D_{3h}$ distortion (78). As just this kind of π -electron delocalization is amenable to manifestations of aromaticity and antiaromaticity, this bears witness to the validity of the structural criteria relying on equalization of the carbon–carbon bond lengths (1, 61, 62, 78, 79). Because the scope of the present publication does not permit me to go into details of this discussion, I refer the reader to the original publications.

Effects of Nonplanarity

A planar molecular structure is usually regarded as a distinguishing feature of the π -aromatic species (1–3), whereas the preferability of a nonplanar structure is often taken as a manifestation of the antiaromaticity of the planar form, which is unstable with respect to out-of-plane distortions (80, 81). A structural criterion of aromaticity and antiaromaticity could be set up on the condition that planar structure is determined above all by the aromaticity of a molecule, whereas antiaromaticity is reflected as nonplanarity of the equilibrium structure.

Convenient models for studying the relationship between the aromaticity of a molecule and the stability of its geometry with respect to out-of-plane distortions are cyclophanes **4**. Calculation of the HSE values has shown that the destabilization of these molecules is directly proportional to the ring-bending angle (82). The calculated HSE values indicate energetic disadvantage of out-of-plane distortions for aromatic molecules, which may cause the loss of aromaticity. This conclusion is supported by calculations of the energy raising that occurs upon folding the benzene ring about the C–1–C–4 axis (81).

However, a question arises. Is such a destabilization chiefly caused by the lessening aromaticity, or is it mainly due to change in the total π -energy, which is minimal when the ring geometry is planar and rises upon out-of-plane distortion? This question has no one simple answer. Moreover, one may not categorically declare that out-of-plane distortions of the benzene ring necessarily involve a substantial diminution of aromaticity.



For example, based on equalization of the bond lengths in the benzene ring, [n]para-cyclophanes ($n = 5–7$) should be classified as aromatic, notwithstanding the

considerable out-of-plane distortions of the benzene ring (1, 82). Another example is given by 8,11-dichloro[5]meta-cyclophane, in which the benzene ring has a strongly bent unsymmetrical boat conformation with the bending angles of 27° and 12° (83). Nevertheless, the bond-length alternation that would point to the loss of aromaticity is not observed and the CC bond lengths in the benzene moiety are equal within experimental accuracy (1.393 ± 0.007 Å). The correlation of the *ortho*-benzylic coupling constants with the square of the bond orders for para-cyclophanes shows that the benzene ring in these species can undergo severe distortions of the σ -framework without disruption of the π -system (84). This agrees with the conclusion that the boat-shaped benzenes with deviations from planarity up to 25° retain the π -conjugation and can be considered as “essentially aromatic compounds” (85). Benzene itself can be slightly folded in the crystal lattice as shown by a very accurate neutron diffraction study (86).

Just as the planar structure of a conjugated cyclic molecule (such as tropone **5** [87]) cannot be regarded as the sufficient condition for conclusion in favor of its aromaticity, a nonplanar structure of the ground state of such a molecule will not be a reliable sign of its antiaromaticity. In each case, an analysis of the factors determining the geometry is required. Cyclobutadiene, the archetypal antiaromatic molecule, has a planar D_{2h} structure, whereas the D_{2d} structure possesses higher energy and does not correspond to a minimum on the PES (88). Cyclooctatetraene has a nonplanar structure of D_{2d} symmetry **6**; however, the π -electron energy of this molecule is minimal for the planar geometry (89, 90). The nonplanar geometry of the carbon skeleton of cyclooctatetraene as well as of its derivatives results from the angular strain arising in the σ -system of the planar configuration. (Its contribution to the enthalpy of the out-of-plane distortion into the D_{2d} structure is $\approx 85\%$ [90].)

A molecular structure classified as antiaromatic can have, however, only slight deviations from planarity, as in 1,5-bis-dehydro[12]annulene (91). 1,4-Dioxin, having 8 π -electrons and formally obeying the $4n$ Hückel rule, has been found to be planar as well (92). On the other hand, specific features of a σ -system may give rise to a nonplanar geometry of a molecule regarded as aromatic. Thus, the dication and dianion of cyclobutadiene, though satisfying the $4n+2$ Hückel rule, possess nonplanar structures as shown by ab initio calculations (93, 94). Aromatic cyclic π electron delocalization does stabilize a planar structure of an aromatic molecule (1, 3). The problem is that, in addition to the aromaticity effect, there may be others that can overshadow it. For example, while the D_{10h} structure of [10]annulene manifests its aromaticity, the σ -skeleton possesses such severe angle strain that this structure is forced to twist (95).

Acknowledgment

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