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On the aromatic stabilization energy of the $4N + 2$ electron pyrene

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RESEARCH ARTICLE

On the aromatic stabilization energy of the $4N$ π electron pyrene

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Abstract

The aromatic stabilization energy (ASE) of pyrene, evaluated with both isodesmic equation and *ab initio* valence bond (VB) theory-based block localized wavefunction (BLW) methods, give consistent results (ca 74 kcal/mol). Biphenyl, phenanthrene and benzene, evaluated similarly, all have essentially the same ASEs per ring carbon. The aromaticity of pyrene is not diminished because of its $4n$ π electron count.

Keywords: pyrene, aromatic stabilization energy, Pauling-Wheland resonance energy, extra cyclic resonance energy, block-localized wavefunction

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1. Introduction

Pyrene, the smallest peri-fused polycyclic aromatic hydrocarbon, has important applications in organic chemistry, the pharmaceutical industry, and materials science due to its rich photochemistry and predictable substitution reactions [1]. This highly symmetrical molecule (point group D_{2h}) can also be viewed as one of the basic graphite and fullerene subunits [2]. Despite having 16 π electrons, pyrene is aromatic based on Clar's sextet [3], Platt's ring perimeter [4], and the Randić–Herndon conjugated circuit [5] models, commonly employed for qualitative characterization of the aromaticity of polycyclic aromatic compounds. Jenneskens et al.'s visualization of the ring current density of pyrene revealed a diatropic circuit predominately along the $4n+2$ π perimeter "which subsumes local benzene-like currents in the two [biphenyl-like] hexagons" [6]. Our companion paper to the present work demonstrated that the aromatic stabilization energy (ASE) [7-9] of the pyrene fragment of a series of increasingly distorted $[n](2,7)$ pyrenophanes is rather insensitive to bending from planarity [10]. The ASE measures the extra stabilization due to cyclic electron delocalization (aromaticity) relative to the stabilization of a conjugated model reference system lacking aromaticity [7-9]. Our previous paper evaluated the *relative* ASEs of distorted $[n](2,7)$ pyrenophanes [10], based on a set of isodesmic equations [11][12] closely related to each other.

However, the "best" absolute value of the ASE of pyrene, as well as its resonance energy (RE) [13], remains unsettled, since different theoretical methods have led to very different numerical results. Note that ASEs [7-9] and REs [13] are conceptually different; REs measure the total stabilization due to π conjugation of the entire system [13], but ASEs measure only the part of the "extra" π stabilization due to aromaticity [7-9]. Even the RE estimates of pyrene vary over 150 kcal/mol! Bird proposed a 141.4 kcal/mol RE based on a bond energy evaluation scheme and experimental heats of formation ($\Delta_f H^\circ_{298}$) [14]. The bond separation resonance energy (BSRE) of pyrene is 218.1 kcal/mol (based on Equation 8, section 3.1). The 62.3 kcal/mol RE value of Jenneskens *et al.*, based on computational *ab initio* VB methods [15], is much less than either of these.

ASE evaluations are just as problematic. Carefully designed isodesmic [11][12] or homodesmotic equations [16] comparing aromatic molecules with non-aromatic but conjugated reference compounds attempt to balance bond types and carbon hybridizations in the reactants and products, but in practice do so to different extents and other "contaminating" energetic imbalances and imperfections may be present [8][17]. Isodesmic equations preserve the number of formal carbon-carbon bond types (single, double or triple) and equal numbers

of each type of carbon atoms (sp^3 , sp^2 or sp) [8][11][18]. Homodesmotic equations, in the least ambiguous definition [18], retain (a) equal numbers of each type of carbon-carbon bonds (Csp^3-Csp^3 , Csp^3-Csp^2 , Csp^2-Csp^2 etc.) and (b) equal numbers of each carbon atom type (sp^3 , sp^2 or sp) with the same number of hydrogens attached [16][18].

Earlier evaluations of the aromatic stabilization of pyrene, isodesmic Equations (1) and (3)) [11][12] and homodesmotic Equation (2) [16c], underestimate the ASE considerably. All three equations suffer from flaws in the choice of reference compounds (which result in unbalanced “perturbing” energetic effects) [8]. Both Equations (1) and (2) can be evaluated using experimental heats of formation ($\Delta_f H^\circ_{298}$) [19]. But Equation (1) estimates the ASE of pyrene by approximating the conjugation reference energy of pyrene with 11 *anti* 1,3-butadienes, although most of the butadiene moieties in pyrene have *syn*, rather than *anti* conformations (see below). Equation (1) also is only isodesmic and has unequal numbers of carbon atoms with zero, one or two hydrogen atoms attached in the reactants and products. George *et al.*’s homodesmotic equation (2) corrected the latter problem [16c], but suffers from other severe imbalances (note that there are six more protobranches [17] on the right side of the equation than on the left). Like Equation (1), Equation (2) (as well as Equation (3), see below) is marred by fundamental *syn-anti* butadiene mismatches [8][9]. As noted above, pyrene has mainly *syn* butadiene subunits, which are inherently less stable (ca. 3.7 kcal/mol each, see below) than the *anti* butadiene conformations in the reference molecules [9]. A further difficulty in using Equations (1) and (2) is the required inclusion of reference molecules many times for stoichiometric balance, as this multiplies errors in the energies of individual molecules [20]. (However, we note that highly accurate computationally-derived data, e.g. now being determined by Allen, Schaefer, et. al. [21], can help reduce this problem.)

Equation (1)

(ASE = +56.4 ± 3.8 kcal/mol; expt.; not corrected for syn-anti mismatches) [19][20]

Equation (2)

(ASE = +47.5 ± 6.8 kcal/mol; expt.; not corrected for syn-anti mismatches) [16c][19][20]

Unlike Equations (1) and (2), the ASE evaluation of pyrene by the isodesmic isomerization stabilization energy (ISE) method (Equation (3)) [12], involves only one closely

related reference molecule. However, the energy of this molecule only is available computationally and it also suffers from *syn-anti* butadiene mismatches [8][9]. The ISE measures the energy difference between a methyl substituted pyrene and its non-aromatic quinoid isomer with an exo-methylene group [9][12]. Methyl substituents have very little effect on the aromaticity of arenes [22], but Equation (3) has energetic imbalances due to hyperconjugation differences as well as unequal numbers of carbon-carbon bond types (Csp^3 - Csp^3 , Csp^3 - Csp^2 , Csp^2 - Csp^2 etc.) and unequal numbers of C, CH, CH_2 , and CH_3 groups.

Equation (3)

(ASE = +58.8 kcal/mol at B3LYP/6-31G* including ZPE; not corrected for *syn-anti* mismatches) [12]

Elaborated isodesmic equations employing *dimethylene* quinoid references largely overcome such problems (see Equation (11) of section 3.2). Thus, quinoid arene reference models with two methylene groups involving only sp^2 -hybridized carbon atoms have been used to evaluate the ASEs of monocyclic as well as large polycyclic aromatic systems [8][10][23]. The ASE of benzene based on 1,4-quinodimethane (29.3 kcal/mol; see Equation (4)) after applying appropriate *syn-anti* mismatch corrections [8][24] is consistent with the recently recommended value (28.8 kcal/mol) based on the homodesmotic Equation (5) [17]. The value based on radialene-like systems (28.7 kcal/mol; see Equation (6)) also is consistent [8]. We propose a similar isodesmic equation, based on a dimethylene-substituted pyrene with appropriate *syn-anti* butadiene mismatch corrections, as a way to evaluate the ASE of pyrene (see Equation (11) of section 3.2).

Equation (4)

(ASE = +29.3 kcal/mol at B3LYP/6-311+G** including ZPE; corrected for three *syn-anti* mismatches)[8][24]

Equation (5)

(ASE = +28.8 kcal/mol; expt.; no correction needed) [8][17]

Equation (6)

(ASE = +28.7 kcal/mol at B3LYP/6-311+G** including ZPE; no correction needed)[8]

ASEs, as well as REs [13], can also be evaluated theoretically through rigorous *ab initio* valence bond (VB) [25] computations [26], without recourse to reference molecules. We adopt the original Pauling-Wheland resonance energy (PWRE) definition [13], which is the difference between the total ground state energy of a conjugated molecule and the energy of its most stable resonance form. Although VB methods are useful in estimating the relative contributions (“weights”) of various Kekulé resonance forms [15], the RE values obtained depend strongly on the types of VB methods, orbitals, and wavefunctions employed (see Table 2 in ref. 27). *Ab initio* VB methods are computationally costly, due to the nonorthogonality of their orbitals and the complexity of their wavefunctions. Instead, we employ a practicable block localized wavefunction (BLW) method [28] to examine the PWRE and ASE of pyrene. The BLW method is a variant of the *ab initio* VB approach, which incorporates both molecular orbital (MO) and VB theories, but is much more efficient due to its MO-based computation.

We demonstrate how the BLW technique can be used to derive the PWREs and ASEs of polycyclic aromatic systems like pyrene, and that the results are consistent with those obtained from logically corrected isodesmic equations. The ASEs and REs of phenanthrene and biphenyl also are computed, for comparison to pyrene. All three compounds have a common “biphenyl” component, encompassing two Clar sextets.

2. Methods

All geometries were optimized with the Gaussian 98 program [29] at the B3LYP/6-311+G** level. Vibrational frequencies, computed at the same level, characterized the

stationary points and gave zero point energies (ZPE). Unscaled ZPE corrections were applied for all energy evaluations. For biphenyl, we compute both the D_2 (NIMAG=0; no imaginary frequency) minimum and the D_{2h} (NIMAG=1) planar transition state, which is only 2.1 kcal/mol higher in energy. Data for the planar form was employed to evaluate the ASE of biphenyl, for comparison with planar phenanthrene and pyrene. Wavefunction instability tests indicated that the quinoid reference compounds had singlet diradical character, e.g., for the dimethylene pyrene isomers: **1** ($\langle S^2 \rangle = 0.79$), **2** ($\langle S^2 \rangle = 1.02$) and **3** ($\langle S^2 \rangle = 1.10$), dimethylene phenanthrene ($\langle S^2 \rangle = 0.64$), and dimethylene biphenyl ($\langle S^2 \rangle = 0.29$). The energetic consequences are discussed below in section 3.2.

Block-localized wavefunction (BLW) [28] computations (followed by geometry optimization) at B3LYP/6-31G* [28h] using the GAMESS (version R5) [30] program, evaluated the adiabatic PWRE [13] and ASE [7-9] of pyrene, biphenyl, and phenanthrene. The PWRE [13] can be derived conveniently via BLW by employing a hypothetical “localized” wavefunction to compute the total energy of the most stable resonance contributor. This is compared with the energy of the completely delocalized ground state structure; the latter is fully optimized by regular MO computations, which, by definition, include all the possible contributing structures. In contrast to the ground state wavefunction, which employs regular delocalized canonical MOs, the BLW wavefunction is constructed from a set of “block-localized” MOs. These are obtained by partitioning electrons and basis functions into several subspaces. Orbitals of the same subspaces are mutually orthogonal but those of different subspaces overlap freely. This procedure “turns off” (disables) the intramolecular interactions among the subgroups that have been selected; the energetic consequence of this operation is evaluated by comparison with the energy of the fully relaxed ground state. The BLW technique is flexible and can be applied to many different types of energy analysis, depending on the nature of the interactions that are “turned off” [28].

3. Results and discussion

3.1. Bond separation resonance energy (BSRE). Isodesmic bond separation resonance energy (BSRE) [11][17] evaluations are the simplest and most direct way to estimate REs based on experimental thermochemical data [19]. BSRE's are uniquely defined, as each of the bonds between the non-hydrogen atoms are separated into the simplest two-heavy atom fragments, e.g., ethane and ethene, while retaining their formal bond types [18]. Hybridization imbalance is the chief concern in unstrained systems. The number of, e.g., Csp^2 -H and Csp^3 -H bonds are not the same on both sides of such equations, and their bond energies differ.

However, for all BSRE equations, there is always twice as many Csp^2 -H/ Csp^3 -H mismatches as there are Csp^2 - Csp^2 / Csp^3 - Csp^3 imbalances. Therefore, such hybridization errors tend to compensate and are likely to be negligibly small in the present context [17]. The difference between Csp^2 -H and Csp^3 -H bond energies, deduced to be about 2 kcal/mol [31], is cancelled in the BSRE equations by the compensating Csp^2 - Csp^2 and Csp^3 - Csp^3 bond energy differences, estimated to be about 4 kcal/mol [32]. For example, the extra six Csp^2 -Hs favoring the right side in the BSRE evaluation of benzene (Equation (7)), is compensated by the advantages of three Csp^2 - Csp^2 bonds favoring the left side (see Equation (7)). Hence, we argue that no energetically significant hybridization imbalance corrections are needed in the present context. The BSRE of benzene, based on Equation (7) and its experimental heat of formation ($\Delta_f H^\circ_{298}$) [19], is 64.6 kcal/mol (see Table 1).

Equation (7)

(BSRE = $+64.6 \pm 1.1$ kcal/mol; expt.; no hybridization correction applied – see text) [17][19]

Similarly, the BSRE of pyrene, based on Equation (8), is 218.1 kcal/mol. The 11 extra Csp^2 - Csp^2 bonds favoring the left side by hybridization compensate the 22 extra Csp^2 -H bonds favoring the right.

Equation (8)

(BSRE = $+218.1 \pm 3.8$ kcal/mol; expt.; no hybridization correction applied – see text) [19]

BSRE values for phenanthrene (180.2 kcal/mol, Equation (9)) and for biphenyl (141.0 kcal/mol, Equation (10)) were evaluated for comparison (Table 1). Following the arguments for benzene and pyrene, hybridization imbalances were considered to be negligible. Although pyrene, phenanthrene, and biphenyl all have two Clar rings, the BSRE per carbon decreases as follows: pyrene (13.6 kcal/mol) > phenanthrene (12.9 kcal/mol) > biphenyl (11.8 kcal/mol) > benzene (10.8 kcal/mol) (see Table 1). This is linearly consistent with the greater number of

conjugations per carbon in pyrene (11 conjugations/16: ratio 0.69), phenanthrene (nine conjugations/14: ratio 0.64), biphenyl (seven conjugations/12: ratio 0.58) and benzene (three conjugations/6: ratio 0.50).

Equation (9)

(BSRE = +180.2 ± 4.0 kcal/mol; expt.; no hybridization correction applied – see text) [19]

Equation (10)

(BSRE = +141.0 ± 2.5 kcal/mol; expt.; no hybridization correction applied – see text) [19]

3.2. Aromatic Stabilization Energy (ASE) Evaluation. We also applied isodesmic Equation (11) to evaluate the ASE of pyrene. Although this equation does not satisfy the homodesmotic requirements [18], there is no hybridization imbalance as all molecules only have sp^2 -carbon atoms. Only pyrene, butadiene, ethylene, and a single quinoidal reference compound (**1**) are involved, but the syn-anti mismatch correction is not straightforward and **1**, like its alternative isomers, **2** and **3** (Figure 2), has singlet biradical wavefunction instability.

Equation (11)

(Uncorrected value: +43.0 kcal/mol at B3LYP/6-311+G** including ZPE; ASE = +74.5 kcal/mol after two Clar ring and five avg mismatch corrections – see text)

While 2,7-dihydro-2,7-dimethylenepyrene (**1**), 2,4-dihydro-2,4-dimethylenepyrene (**2**) and 4,9-dihydro-4,9-dimethylenepyrene (**3**) all have enforced quinoidal structures, the topologies of their single and double bond localizations are rather different (see Figure 2). Compound **1** possesses 12 *anti* butadiene moieties, **2** involves nine *anti* and three *syn*, **3**

includes six *anti* and six *syn*. All three have significant singlet biradical instabilities (see Methods). The energy differences between the restricted singlet and unrestricted biradical singlet states are $\Delta E = 4.0$ kcal/mol for **1**, 8.7 kcal/mol for **2**, and 14.8 kcal/mol for **3**. Both **2** and **3** have non-planar minima but have negligible planarization energies (both are less than 0.1 kcal/mol).

Since **1**, the most stable quinoid reference isomer, has a planar (D_{2h}) minimum and the smallest (and rather insignificant) singlet biradical instability, its closed shell total singlet energy has been employed in Equation (11). This reaction is 43.0 kcal/mol endothermic as written, but *syn-anti* butadiene mismatch corrections need to be applied. These corrections arise since, unlike all-*anti* **1**, pyrene is comprised mostly of *syn* diene conformations. Hence, the total correction must take into account the increase in the number of *anti* diene units, worth 3.7 kcal/mol each [24], in going from the left to the right side of Equation (11).

As the formal structures of the six leading pyrene resonance contributors (see Figure 1) have different number of *syn* moieties, varying from five to nine, the selection is somewhat arbitrary. Hence, we propose a general and more objective selection procedure. First, resonance contributors with the largest number of Clar rings are chosen. This eliminates contributors (5) and (6) for pyrene. Each Clar ring is represented with the circle notation and is assigned three *syn* conformations. Thus, when compared to anti-butadiene reference molecules, three *syn-anti* mismatch corrections (3.7 kcal/mol each, total 11.1 kcal/mol) for benzene are needed for each Clar ring. However, with regard to the rest of the molecule, the two Kekulé resonance contributors of each Clar ring are not considered separately (in the *syn* vs. *anti* sense), but are averaged. Thus, Clar ring interactions with the other moieties are neither *syn* nor *anti*, but are treated as an average (“*avg*”) of both, corresponding to half a *syn* correction (1.9 kcal/mol). Using this procedure, biphenyl (compared to anti-butadiene reference molecules) requires a total of 6.5 *syn-anti* mismatch corrections (two Clar rings and one *avg*). On this basis, phenanthrene would require 7.5 *syn-anti* mismatch corrections (two Clar rings and three *avg*).

This correction procedure, when applied to pyrene in Equation (11), involving two Clar rings and five *avg* (8.5 *syn-anti* mismatch corrections), gives an ASE of 74.5 kcal/mol. Remarkably, this value approaches 16/6 the ASE of benzene based on Equation (4) ($29.3 \times (16/6) = 78.1$ kcal/mol) [8][33]. The 74.5 kcal/mol value for the ASE of pyrene may be compared to the stabilization energies of planar biphenyl (D_{2h} symmetry) and phenanthrene (all three systems have two Clar sextets) (see Table 1). Based on Equation (12) and the same correction procedure (see above), D_{2h} biphenyl has ASE = 58.3 kcal/mol (6.5 *syn-anti*

mismatches), which is roughly twice the ASE of benzene ($29.3 \times (12/6) = 58.6$ kcal/mol). The energy difference between the D_2 minimum and D_{2h} planar transition state of biphenyl is only 2.1 kcal/mol, but the latter resembles the biphenyl moiety of pyrene more closely.

Experimentally, phenanthrene is *ca.* 7 kcal/mol more stable than its $4n+2$ π electron isomer, anthracene (which has only one Clar ring) [19][34][35]. Phenanthrene also is stabilized to a similar extent per π electron as benzene [36]. Our phenanthrene ASE (66.6 kcal/mol based on Equation (13) and including 7.5 *syn-anti* mismatches, see above) is close to $14/6$ the ASE of benzene ($29.3 \times 14/6 = 68.4$ kcal/mol). Both the quinoid dimethylene phenanthrene (Equation (13)) and dimethylene biphenyl (Equation (12)) reference molecules have singlet biradical instabilities (see Methods section), but the energy differences between their restricted singlet and unrestricted biradical singlet states are small (*ca.* 2.6 kcal/mol and 1.2 kcal/mol, respectively).

Equation (12)

(Uncorrected value: +34.2 kcal/mol at B3LYP/6-311+G** including ZPE; ASE = +58.3 kcal/mol after two Clar ring and one *avg* mismatch corrections – see text)

Equation (13)

(Uncorrected value: +38.8 kcal/mol at B3LYP/6-311+G** including ZPE; ASE = +66.6 kcal/mol after two Clar and three *avg* mismatch corrections – see text)

As documented above, pyrene, biphenyl, and phenanthrene are all stabilized by aromaticity to a similar extent per π electron. This is shown directly by the homodesmotic disproportion reaction, Equation (14), which, when evaluated with the experimental heats of formation ($\Delta_f H^\circ_{298}$), is thermoneutral within experimental error ($+1.2 \pm 2.7$ kcal/mol) [19]. Likewise, the corrected ASEs computed for pyrene, phenanthrene and biphenyl also predict essential thermoneutrality (+0.4 kcal/mol). Note also that the wavefunction instability errors of the ASEs of pyrene (4.0 kcal/mol), phenanthrene (2.6 kcal/mol) and biphenyl (1.2

kcal/mol), evaluated based on Equations (11)-(13), largely cancel in Equation (14). Thus, we conclude that the aromaticity of pyrene is not reduced because of its $4n\pi$ electron count.

Equation (14)

($+1.2 \pm 2.7$ kcal/mol; expt. $\Delta_f H^\circ_{298}$; no corrections. Our ASE values give $+0.4$ kcal/mol.)

3.3. Block Localized Wavefunction (BLW) Evaluations. ASEs also can be evaluated computationally by employing the specifically designed BLW [28] method to estimate the PWREs [13] (see Methods section) of the arene as well as the conjugated olefin reference compounds chosen for comparison. This procedure does not employ the total energies of these molecules, but only uses the PWREs to derive “extra cyclic resonance energies” (ECREs). The ECRE measures the greater stabilization associated with the “aromatic” cyclic π electron delocalization of a fully conjugated ring system [37]. ECREs are closely related to ASEs (which are based on evaluations using experimental heats of formation or analogous computed total energies), but have considerable advantages, both conceptually and in practice.

The procedure used to evaluate ECREs largely cancels perturbing energetic effects other than aromaticity, for example ring strain and hybridization imbalance. Thus, the ECRE = 29.3 kcal/mol of benzene, obtained from the energy difference between the PWRE of benzene (61.4 kcal/mol) and that of three *syn* butadienes (PWRE = 10.7 kcal/mol each), is comparable to the ca. 29 kcal/mol ASE values for benzene derived and discussed above (see Equations (4), (5) and (6)). The PWRE for benzene (61.4 kcal/mol) also is close to the experimentally-derived BSRE value (64.6 kcal/mol, see Equation 7). However, this ECRE procedure cannot be applied as straightforwardly to the pyrene ECRE evaluation. Pyrene can be represented by six resonance contributors with one or two Clar rings and different numbers of formal *syn*/anti butadiene moieties (see Figure 1).

Our choice is based on our “avg” procedure (proposed in section 3.2) for correcting the *syn*/anti mismatches of ASE Equations (11)-(13), we first select the resonance contributors with the most Clar rings (e.g. contributors 1–4 for pyrene, Figure 1) and eliminate the rest (e.g. for pyrene, contributors 5 and 6, see Figure 1). For pyrene, each Clar moiety represents three *syn* butadienes. The remaining butadiene moieties of the Kekule structures, which

interact with the top and bottom Clar rings but are neither *syn* nor *anti*, are assigned five *syn/anti* averaged (*avg*) butadiene moieties. Thus, the ECRE of pyrene (74.5 kcal/mol) is given by the energy difference between the PWRE of pyrene (196.2 kcal/mol) relative to the PWRE sum of six *syn* (2 Clar rings, PWRE = 32.1 kcal/mol for each Clar ring) and five *avg* butadienes (*avg* butadiene PWRE = $(10.7 \text{ (syn)} + 12.2 \text{ (anti)})/2 = 11.5$ kcal/mol each). This ECRE value (74.5 kcal/mol) is in excellent agreement with the ASE (74.5 kcal/mol) derived for pyrene from Equation (11). The PWRE value of pyrene given by BLW (196.2 kcal/mol) is of the same magnitude as its BSRE value (218.1 kcal/mol, Equation (8), see section 3.1); both are much larger than the RE given by Jenneskens, et al. [15].

Note that ECREs depend on the formal canonical structure selected for two reasons. First, the BLW energies, computed for various localizations corresponding to the formal structures of individual resonance contributors, differ (as they should). However, these differences, e.g., as shown in Figure 1, are small. Second, the number of *syn-anti* butadiene reference moieties differs for the various canonical forms (as discussed above). Each localization scheme leads to a different ECRE value, but those having the same number of Clar sextet rings give similar values. Specifically, the ECREs based on pairs of equivalent contributors 1, 2 (74.5 kcal/mol) and 3, 4 (75.1 kcal/mol) (both have two Clar sextets) are close in energy. We chose the ECRE of the canonical structure (contributors 1 and 2) with the greatest number of formal *syn* butadiene units, since the PWRE difference between contributors 1–4 are negligible (see Figure 1). In agreement with Bird's comparative evaluation [14] and the VB-based computations of Jenneskens *et al.* [15], the relative importance of contributors 1–4 are greater than contributors 5 and 6.

Based on the same BLW procedure, we computed PWREs of D_{2h} biphenyl (133.0 kcal/mol) [38] and phenanthrene (165.2 kcal/mol). These data are in line with, but smaller than their BSRE values (biphenyl: 141.0 kcal/mol, Equation (10); phenanthrene: 180.2 kcal/mol, Equation (9)). The ECREs of biphenyl (57.3 kcal/mol) and phenanthrene (66.7 kcal/mol), based on their resonance canonical forms with the greatest number of *syn* butadiene units, agree with their *syn-anti* corrected ASE values given by Equations (12) and (13) (see Table 1). Based on the same ECRE procedure applied for pyrene, the ECRE of phenanthrene is derived from the PWRE of phenanthrene relative to the PWRE sum of six *syn* (10.7 kcal/mol each) and three *avg* (11.5 kcal/mol each) butadienes. The ECRE of biphenyl is derived from the PWRE difference between biphenyl and the sum of six *syn* and one *avg* butadiene. The ECREs per ring carbon of biphenyl (4.8 kcal/mol), phenanthrene (4.8 kcal/mol) and pyrene (4.7 kcal/mol) are almost the same as that of benzene (4.9 kcal/mol) (see

Table 1). Although stabilized by aromaticity to a similar extent, the overall PWRE, per ring carbon, of pyrene, phenanthrene, biphenyl and benzene, decreases in the following order: pyrene (12.3 kcal/mol) > phenanthrene (11.8 kcal/mol) > biphenyl (11.1 kcal/mol) > benzene (10.2 kcal/mol). Note that PWREs measure the total stabilization of a molecule, which includes interactions not evaluated in ECRE estimates. Biphenyl is a good example, since its PWRE (but not the ECRE) includes the non-Clar conjugation (*ca.* 11 kcal/mol, similar to that of butadiene) between the two Clar rings. Thus, the PWRE of biphenyl is more than twice that of benzene (see Table 1). Likewise, the PWREs of phenanthrene and pyrene also include non-Clar conjugative interactions.

4. Conclusion

Isodesmic or homodesmotic equations employed for aromatic stabilization energy (ASE) and resonance energy (RE) evaluations for polycyclic arenes are difficult to devise to isolate the desired energetic effects as the reference molecules often are complicated by other perturbing influences. However, isodesmic bond separation resonance energy (BSRE) evaluations of strain-free arenes are non-arbitrary, well-defined, use simple reference molecules for which experimental data are available, and the drawback of inherent hybridization imbalance may largely be compensated. The BLW method provides a general, direct approach for evaluating Pauling–Wheland REs, as no additional reference compounds, other than the system itself, is needed.

ASE evaluations are inherently more complex as they require comparisons with conjugated, but non-aromatic reference systems, which seldom are free from other complicating energetic effects. ASE evaluations of unstrained arenes may employ butadiene as the smallest π conjugated reference model. However, *syn*-butadiene, rather than its 3.7 kcal/mol more stable *anti*-butadiene isomer, represents the predominant conformation in arenes. Thus, benzene requires three *syn*-butadiene models. Polycyclic aromatics incorporate *syn*- but also *avg* (averaged) butadiene moieties. The extra cyclic resonance energies (ECREs, akin to ASEs) can also be derived by comparing the BLW computed PWRE of the aromatic molecule with the PWRE of the chosen reference system. Other energetic effects do not perturb such comparison.

Based on both ASE and ECRE evaluations, the aromatic stabilization per ring carbon of biphenyl, phenanthrene, pyrene, and benzene are all nearly the same. Hence, the aromaticity of pyrene is not diminished because of its $4n$ π electron count. In contrast, both the PWRE and the BSRE values *per carbon* increase in going from benzene to biphenyl, due

to the extra conjugation between the two phenyl rings. Phenanthrene and especially pyrene benefit even more from such extra non-Clar conjugation. These non-Clar conjugations are not taken into account in the ECRE and ASE estimates, but are included when evaluating the total stabilization of molecules, based on their PWREs and BSREs.

Acknowledgements

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But since pyrene, with 10 CH's and 6 C's, has different groups from benzene (6 CH's), this has little relevance in the ASE context. We note that the heat of formation per carbon of the non-aromatic diamond is nearly the same as that for the highly aromatic graphite.

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	Contributor 1 9 <i>syn</i> 2 <i>anti</i> or 2 Clar 5 <i>avg</i>	Contributor 2 9 <i>syn</i> 2 <i>anti</i> or 2 Clar 5 <i>avg</i>	Contributor 3 8 <i>syn</i> 3 <i>anti</i> or 2 Clar 5 <i>avg</i>	Contributor 4 8 <i>syn</i> 3 <i>anti</i> or 2 Clar 5 <i>avg</i>	Contributor 5 5 <i>syn</i> 6 <i>anti</i> or 1 Clar 2 <i>syn</i> 2 <i>anti</i> 4 <i>avg</i>	Contributor 6 5 <i>syn</i> 6 <i>anti</i> or 1 Clar 2 <i>syn</i> 2 <i>anti</i> 4 <i>avg</i>
BLW PWRE (in kcal/mol)	196.2	196.2	196.8	196.8	194.8	194.8
ECRE (in kcal/mol)	74.5	74.5	75.1	75.1	70.9	70.9

Figure 1. BLW computed PWREs and ECREs (at B3LYP/6-31G*) of different pyrene resonance contributors. The formal number of *syn* and *anti* butadiene moieties of each contributor (1-6) are given below each structure. The PWREs are computed directly, but the ECREs of each of the resonance contributors are derived from the PWRE of the resonance contributor itself relative to the sum of the PWREs of the assigned number of Clar and type of butadiene references that represents the specific resonance contributor ($10.7 \times 3 = 32.1$ kcal/mol for each Clar ring and 11.5 kcal/mol for each *syn/anti* averaged butadiene). For example, the ECRE of Contributor 1 and 2 is $196.2 - (2 \times 32.1 + 5 \times 11.5) = 74.5$ kcal/mol.

	1	2	3
Total energy of closed shell singlet including ZPE (Hartrees)	-693.03269	-693.02335	-693.01290
Total energy of biradical including ZPE (Hartrees)	-693.03913	-693.03717	-693.03653
$\langle S^2 \rangle$	0.79	1.02	1.10
Relative energy of closed vs. open shell singlet (kcal/mol)	4.0	8.7	14.8
Planarization Energy (kcal/mol)	0.0	0.0	0.1
ASE based on Equation (11) including ZPE (kcal/mol)	43.0	48.9	55.4
Total number of anti-butadiene subunits	12	9	6
Number of syn-anti correction (3.7 kcal/mol each)	8.5	5.5	2.5
ASE after syn-anti correction (kcal/mol)	74.5	69.3	64.7

Figure 2. Dihydrodimethylene-substituted dihydroquinoialpyrene references (**1**, **2** and **3**) employed in Equation (11) for the pyrene ASE evaluation. The ASE values presented in row six are uncorrected. Row nine presents the ASE value after appropriate syn-anti butadiene mismatch correction (the number of corrections applied are indicated in row eight). All data were computed at the B3LYP/6-311+G** level including ZPE.

Table 1. ASE (corrected for syn-anti butadiene mismatches, based on the appropriate homodesmotic equations evaluated at the B3LYP/6-311+G** level, see text), ECRE (BLW), PWRE (BLW) and experimental BSRE values of pyrene, phenanthrene, biphenyl and benzene. All BLW data were computed at the B3LYP/6-31G* level.

	Pyrene	Phenanthrene	Biphenyl (D_{2h})	Benzene
ASE (kcal/mol)	74.5	66.6	58.3	29.3
ASE per ring carbon (kcal/mol)	4.7	4.8	4.9	4.9
ECRE (kcal/mol)	74.5	66.7	57.3	29.3
ECRE per ring carbon (kcal/mol)	4.7	4.8	4.8	4.9
PWRE (kcal/mol)	196.2	165.2	133.0	61.4
PWRE per ring carbon (kcal/mol)	12.3	11.8	11.1	10.2
BSRE (kcal/mol)	218.1	180.2	141.0	64.6
BSRE per ring (kcal/mol)	13.6	12.9	11.8	10.8

RESEARCH ARTICLE

On the aromatic stabilization energy of the $4N$ π electron pyrene

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Abstract

The aromatic stabilization energy (ASE) of pyrene, evaluated with both isodesmic equation and *ab initio* valence bond (VB) theory-based block localized wavefunction (BLW) methods, give consistent results (ca 74 kcal/mol). Biphenyl, phenanthrene and benzene, evaluated similarly, all have essentially the same ASEs per ring carbon. The aromaticity of pyrene is not diminished because of its $4n$ π electron count.

Keywords: pyrene, aromatic stabilization energy, Pauling-Wheland resonance energy, extra cyclic resonance energy, block-localized wavefunction

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1. Introduction

Pyrene, the smallest peri-fused polycyclic aromatic hydrocarbon, has important applications in organic chemistry, the pharmaceutical industry, and materials science due to its rich photochemistry and predictable substitution reactions [1]. This highly symmetrical molecule (point group D_{2h}) can also be viewed as one of the basic graphite and fullerene subunits [2]. Despite having 16 π electrons, pyrene is aromatic based on Clar's sextet [3], Platt's ring perimeter [4], and the Randić–Herndon conjugated circuit [5] models, commonly employed for qualitative characterization of the aromaticity of polycyclic aromatic compounds. Jenneskens et al.'s visualization of the ring current density of pyrene revealed a diatropic circuit predominately along the $4n+2$ π perimeter "which subsumes local benzene-like currents in the two [biphenyl-like] hexagons" [6]. Our companion paper to the present work demonstrated that the aromatic stabilization energy (ASE) [7-9] of the pyrene fragment of a series of increasingly distorted $[n](2,7)$ pyrenophanes is rather insensitive to bending from planarity [10]. The ASE measures the extra stabilization due to cyclic electron delocalization (aromaticity) relative to the stabilization of a conjugated model reference system lacking aromaticity [7-9]. Our previous paper evaluated the *relative* ASEs of distorted $[n](2,7)$ pyrenophanes [10], based on a set of isodesmic equations [11][12] closely related to each other.

However, the "best" absolute value of the ASE of pyrene, as well as its resonance energy (RE) [13], remains unsettled, since different theoretical methods have led to very different numerical results. Note that ASEs [7-9] and REs [13] are conceptually different; REs measure the total stabilization due to π conjugation of the entire system [13], but ASEs measure only the part of the "extra" π stabilization due to aromaticity [7-9]. Even the RE estimates of pyrene vary over 150 kcal/mol! Bird proposed a 141.4 kcal/mol RE based on a bond energy evaluation scheme and experimental heats of formation ($\Delta_f H^\circ_{298}$) [14]. The bond separation resonance energy (BSRE) of pyrene is 218.1 kcal/mol (based on Equation 8, section 3.1). The 62.3 kcal/mol RE value of Jenneskens *et al.*, based on computational *ab initio* VB methods [15], is much less than either of these.

ASE evaluations are just as problematic. Carefully designed isodesmic [11][12] or homodesmotic equations [16] comparing aromatic molecules with non-aromatic but conjugated reference compounds attempt to balance bond types and carbon hybridizations in the reactants and products, but in practice do so to different extents and other "contaminating" energetic imbalances and imperfections may be present [8][17]. Isodesmic equations preserve the number of formal carbon-carbon bond types (single, double or triple) and equal numbers

of each type of carbon atoms (sp^3 , sp^2 or sp) [8][11][18]. Homodesmotic equations, in the least ambiguous definition [18], retain (a) equal numbers of each type of carbon-carbon bonds (Csp^3-Csp^3 , Csp^3-Csp^2 , Csp^2-Csp^2 etc.) and (b) equal numbers of each carbon atom type (sp^3 , sp^2 or sp) with the same number of hydrogens attached [16][18].

Earlier evaluations of the aromatic stabilization of pyrene, isodesmic Equations (1) and (3)) [11][12] and homodesmotic Equation (2) [16c], underestimate the ASE considerably. All three equations suffer from flaws in the choice of reference compounds (which result in unbalanced “perturbing” energetic effects) [8]. Both Equations (1) and (2) can be evaluated using experimental heats of formation ($\Delta_f H^\circ_{298}$) [19]. But Equation (1) estimates the ASE of pyrene by approximating the conjugation reference energy of pyrene with 11 *anti* 1,3-butadienes, although most of the butadiene moieties in pyrene have *syn*, rather than *anti* conformations (see below). Equation (1) also is only isodesmic and has unequal numbers of carbon atoms with zero, one or two hydrogen atoms attached in the reactants and products. George *et al.*’s homodesmotic equation (2) corrected the latter problem [16c], but suffers from other severe imbalances (note that there are six more protobranches [17] on the right side of the equation than on the left). Like Equation (1), Equation (2) (as well as Equation (3), see below) is marred by fundamental *syn-anti* butadiene mismatches [8][9]. As noted above, pyrene has mainly *syn* butadiene subunits, which are inherently less stable (ca. 3.7 kcal/mol each, see below) than the *anti* butadiene conformations in the reference molecules [9]. A further difficulty in using Equations (1) and (2) is the required inclusion of reference molecules many times for stoichiometric balance, as this multiplies errors in the energies of individual molecules [20]. (However, we note that highly accurate computationally-derived data, e.g. now being determined by Allen, Schaefer, et. al. [21], can help reduce this problem.)

Equation (1)

(ASE = $+56.4 \pm 3.8$ kcal/mol; expt.; not corrected for *syn-anti* mismatches) [19][20]

Equation (2)

(ASE = $+47.5 \pm 6.8$ kcal/mol; expt.; not corrected for *syn-anti* mismatches) [16c][19][20]

Unlike Equations (1) and (2), the ASE evaluation of pyrene by the isodesmic isomerization stabilization energy (ISE) method (Equation (3)) [12], involves only one closely

related reference molecule. However, the energy of this molecule only is available computationally and it also suffers from *syn-anti* butadiene mismatches [8][9]. The ISE measures the energy difference between a methyl substituted pyrene and its non-aromatic quinoid isomer with an exo-methylene group [9][12]. Methyl substituents have very little effect on the aromaticity of arenes [22], but Equation (3) has energetic imbalances due to hyperconjugation differences as well as unequal numbers of carbon-carbon bond types (Csp^3 - Csp^3 , Csp^3 - Csp^2 , Csp^2 - Csp^2 etc.) and unequal numbers of C, CH, CH_2 , and CH_3 groups.

Equation (3)

(ASE = +58.8 kcal/mol at B3LYP/6-31G* including ZPE; not corrected for *syn-anti* mismatches) [12]

Elaborated isodesmic equations employing *dimethylene* quinoid references largely overcome such problems (see Equation (11) of section 3.2). Thus, quinoid arene reference models with two methylene groups involving only sp^2 -hybridized carbon atoms have been used to evaluate the ASEs of monocyclic as well as large polycyclic aromatic systems [8][10][23]. The ASE of benzene based on 1,4-quinodimethane (29.3 kcal/mol; see Equation (4)) after applying appropriate *syn-anti* mismatch corrections [8][24] is consistent with the recently recommended value (28.8 kcal/mol) based on the homodesmotic Equation (5) [17]. The value based on radialene-like systems (28.7 kcal/mol; see Equation (6)) also is consistent [8]. We propose a similar isodesmic equation, based on a dimethylene-substituted pyrene with appropriate *syn-anti* butadiene mismatch corrections, as a way to evaluate the ASE of pyrene (see Equation (11) of section 3.2).

Equation (4)

(ASE = +29.3 kcal/mol at B3LYP/6-311+G** including ZPE; corrected for three *syn-anti* mismatches)[8][24]

Equation (5)

(ASE = +28.8 kcal/mol; expt.; no correction needed) [8][17]

Equation (6)

(ASE = +28.7 kcal/mol at B3LYP/6-311+G** including ZPE; no correction needed)[8]

ASEs, as well as REs [13], can also be evaluated theoretically through rigorous *ab initio* valence bond (VB) [25] computations [26], without recourse to reference molecules. We adopt the original Pauling-Wheland resonance energy (PWRE) definition [13], which is the difference between the total ground state energy of a conjugated molecule and the energy of its most stable resonance form. Although VB methods are useful in estimating the relative contributions (“weights”) of various Kekulé resonance forms [15], the RE values obtained depend strongly on the types of VB methods, orbitals, and wavefunctions employed (see Table 2 in ref. 27). *Ab initio* VB methods are computationally costly, due to the nonorthogonality of their orbitals and the complexity of their wavefunctions. Instead, we employ a practicable block localized wavefunction (BLW) method [28] to examine the PWRE and ASE of pyrene. The BLW method is a variant of the *ab initio* VB approach, which incorporates both molecular orbital (MO) and VB theories, but is much more efficient due to its MO-based computation.

We demonstrate how the BLW technique can be used to derive the PWREs and ASEs of polycyclic aromatic systems like pyrene, and that the results are consistent with those obtained from logically corrected isodesmic equations. The ASEs and REs of phenanthrene and biphenyl also are computed, for comparison to pyrene. All three compounds have a common “biphenyl” component, encompassing two Clar sextets.

2. Methods

All geometries were optimized with the Gaussian 98 program [29] at the B3LYP/6-311+G** level. Vibrational frequencies, computed at the same level, characterized the

stationary points and gave zero point energies (ZPE). Unscaled ZPE corrections were applied for all energy evaluations. For biphenyl, we compute both the D_2 (NIMAG=0; no imaginary frequency) minimum and the D_{2h} (NIMAG=1) planar transition state, which is only 2.1 kcal/mol higher in energy. Data for the planar form was employed to evaluate the ASE of biphenyl, for comparison with planar phenanthrene and pyrene. Wavefunction instability tests indicated that the quinoid reference compounds had singlet diradical character, e.g., for the dimethylene pyrene isomers: **1** ($\langle S^2 \rangle = 0.79$), **2** ($\langle S^2 \rangle = 1.02$) and **3** ($\langle S^2 \rangle = 1.10$), dimethylene phenanthrene ($\langle S^2 \rangle = 0.64$), and dimethylene biphenyl ($\langle S^2 \rangle = 0.29$). The energetic consequences are discussed below in section 3.2.

Block-localized wavefunction (BLW) [28] computations (followed by geometry optimization) at B3LYP/6-31G* [28h] using the GAMESS (version R5) [30] program, evaluated the adiabatic PWRE [13] and ASE [7-9] of pyrene, biphenyl, and phenanthrene. The PWRE [13] can be derived conveniently via BLW by employing a hypothetical “localized” wavefunction to compute the total energy of the most stable resonance contributor. This is compared with the energy of the completely delocalized ground state structure; the latter is fully optimized by regular MO computations, which, by definition, include all the possible contributing structures. In contrast to the ground state wavefunction, which employs regular delocalized canonical MOs, the BLW wavefunction is constructed from a set of “block-localized” MOs. These are obtained by partitioning electrons and basis functions into several subspaces. Orbitals of the same subspaces are mutually orthogonal but those of different subspaces overlap freely. This procedure “turns off” (disables) the intramolecular interactions among the subgroups that have been selected; the energetic consequence of this operation is evaluated by comparison with the energy of the fully relaxed ground state. The BLW technique is flexible and can be applied to many different types of energy analysis, depending on the nature of the interactions that are “turned off” [28].

3. Results and discussion

3.1. Bond separation resonance energy (BSRE). Isodesmic bond separation resonance energy (BSRE) [11][17] evaluations are the simplest and most direct way to estimate REs based on experimental thermochemical data [19]. BSRE's are uniquely defined, as each of the bonds between the non-hydrogen atoms are separated into the simplest two-heavy atom fragments, e.g., ethane and ethene, while retaining their formal bond types [18]. Hybridization imbalance is the chief concern in unstrained systems. The number of, e.g., Csp^2 -H and Csp^3 -H bonds are not the same on both sides of such equations, and their bond energies differ.

However, for all BSRE equations, there is always twice as many Csp^2 -H/ Csp^3 -H mismatches as there are Csp^2 - Csp^2 / Csp^3 - Csp^3 imbalances. Therefore, such hybridization errors tend to compensate and are likely to be negligibly small in the present context [17]. The difference between Csp^2 -H and Csp^3 -H bond energies, deduced to be about 2 kcal/mol [31], is cancelled in the BSRE equations by the compensating Csp^2 - Csp^2 and Csp^3 - Csp^3 bond energy differences, estimated to be about 4 kcal/mol [32]. For example, the extra six Csp^2 -Hs favoring the right side in the BSRE evaluation of benzene (Equation (7)), is compensated by the advantages of three Csp^2 - Csp^2 bonds favoring the left side (see Equation (7)). Hence, we argue that no energetically significant hybridization imbalance corrections are needed in the present context. The BSRE of benzene, based on Equation (7) and its experimental heat of formation ($\Delta_f H^\circ_{298}$) [19], is 64.6 kcal/mol (see Table 1).

Equation (7)

(BSRE = +64.6 ± 1.1 kcal/mol; expt.; no hybridization correction applied – see text) [17][19]

Similarly, the BSRE of pyrene, based on Equation (8), is 218.1 kcal/mol. The 11 extra Csp^2 - Csp^2 bonds favoring the left side by hybridization compensate the 22 extra Csp^2 -H bonds favoring the right.

Equation (8)

(BSRE = +218.1 ± 3.8 kcal/mol; expt.; no hybridization correction applied – see text) [19]

BSRE values for phenanthrene (180.2 kcal/mol, Equation (9)) and for biphenyl (141.0 kcal/mol, Equation (10)) were evaluated for comparison (Table 1). Following the arguments for benzene and pyrene, hybridization imbalances were considered to be negligible. Although pyrene, phenanthrene, and biphenyl all have two Clar rings, the BSRE per carbon decreases as follows: pyrene (13.6 kcal/mol) > phenanthrene (12.9 kcal/mol) > biphenyl (11.8 kcal/mol) > benzene (10.8 kcal/mol) (see Table 1). This is linearly consistent with the greater number of

conjugations per carbon in pyrene (11 conjugations/16: ratio 0.69), phenanthrene (nine conjugations/14: ratio 0.64), biphenyl (seven conjugations/12: ratio 0.58) and benzene (three conjugations/6: ratio 0.50).

Equation (9)

(BSRE = $+180.2 \pm 4.0$ kcal/mol; expt.; no hybridization correction applied – see text) [19]

Equation (10)

(BSRE = $+141.0 \pm 2.5$ kcal/mol; expt.; no hybridization correction applied – see text) [19]

3.2. Aromatic Stabilization Energy (ASE) Evaluation. We also applied isodesmic Equation (11) to evaluate the ASE of pyrene. Although this equation does not satisfy the homodesmotic requirements [18], there is no hybridization imbalance as all molecules only have sp^2 -carbon atoms. Only pyrene, butadiene, ethylene, and a single quinoidal reference compound (**1**) are involved, but the syn-anti mismatch correction is not straightforward and **1**, like its alternative isomers, **2** and **3** (Figure 2), has singlet biradical wavefunction instability.

Equation (11)

(Uncorrected value: $+43.0$ kcal/mol at B3LYP/6-311+G** including ZPE; ASE = $+74.5$ kcal/mol after two Clar ring and five avg mismatch corrections – see text)

While 2,7-dihydro-2,7-dimethylenepyrene (**1**), 2,4-dihydro-2,4-dimethylenepyrene (**2**) and 4,9-dihydro-4,9-dimethylenepyrene (**3**) all have enforced quinoidal structures, the topologies of their single and double bond localizations are rather different (see Figure 2). Compound **1** possesses 12 *anti* butadiene moieties, **2** involves nine *anti* and three *syn*, **3**

includes six *anti* and six *syn*. All three have significant singlet biradical instabilities (see Methods). The energy differences between the restricted singlet and unrestricted biradical singlet states are $\Delta E = 4.0$ kcal/mol for **1**, 8.7 kcal/mol for **2**, and 14.8 kcal/mol for **3**. Both **2** and **3** have non-planar minima but have negligible planarization energies (both are less than 0.1 kcal/mol).

Since **1**, the most stable quinoid reference isomer, has a planar (D_{2h}) minimum and the smallest (and rather insignificant) singlet biradical instability, its closed shell total singlet energy has been employed in Equation (11). This reaction is 43.0 kcal/mol endothermic as written, but *syn-anti* butadiene mismatch corrections need to be applied. These corrections arise since, unlike all-*anti* **1**, pyrene is comprised mostly of *syn* diene conformations. Hence, the total correction must take into account the increase in the number of *anti* diene units, worth 3.7 kcal/mol each [24], in going from the left to the right side of Equation (11).

As the formal structures of the six leading pyrene resonance contributors (see Figure 1) have different number of *syn* moieties, varying from five to nine, the selection is somewhat arbitrary. Hence, we propose a general and more objective selection procedure. First, resonance contributors with the largest number of Clar rings are chosen. This eliminates contributors (5) and (6) for pyrene. Each Clar ring is represented with the circle notation and is assigned three *syn* conformations. Thus, when compared to anti-butadiene reference molecules, three *syn-anti* mismatch corrections (3.7 kcal/mol each, total 11.1 kcal/mol) for benzene are needed for each Clar ring. However, with regard to the rest of the molecule, the two Kekulé resonance contributors of each Clar ring are not considered separately (in the *syn* vs. *anti* sense), but are averaged. Thus, Clar ring interactions with the other moieties are neither *syn* nor *anti*, but are treated as an average (“*avg*”) of both, corresponding to half a *syn* correction (1.9 kcal/mol). Using this procedure, biphenyl (compared to anti-butadiene reference molecules) requires a total of 6.5 *syn-anti* mismatch corrections (two Clar rings and one *avg*). On this basis, phenanthrene would require 7.5 *syn-anti* mismatch corrections (two Clar rings and three *avg*).

This correction procedure, when applied to pyrene in Equation (11), involving two Clar rings and five *avg* (8.5 *syn-anti* mismatch corrections), gives an ASE of 74.5 kcal/mol. Remarkably, this value approaches 16/6 the ASE of benzene based on Equation (4) ($29.3 \times (16/6) = 78.1$ kcal/mol) [8][33]. The 74.5 kcal/mol value for the ASE of pyrene may be compared to the stabilization energies of planar biphenyl (D_{2h} symmetry) and phenanthrene (all three systems have two Clar sextets) (see Table 1). Based on Equation (12) and the same correction procedure (see above), D_{2h} biphenyl has ASE = 58.3 kcal/mol (6.5 *syn-anti*

mismatches), which is roughly twice the ASE of benzene ($29.3 \times (12/6) = 58.6$ kcal/mol). The energy difference between the D_2 minimum and D_{2h} planar transition state of biphenyl is only 2.1 kcal/mol, but the latter resembles the biphenyl moiety of pyrene more closely.

Experimentally, phenanthrene is *ca.* 7 kcal/mol more stable than its $4n+2$ π electron isomer, anthracene (which has only one Clar ring) [19][34][35]. Phenanthrene also is stabilized to a similar extent per π electron as benzene [36]. Our phenanthrene ASE (66.6 kcal/mol based on Equation (13) and including 7.5 *syn-anti* mismatches, see above) is close to 14/6 the ASE of benzene ($29.3 \times 14/6 = 68.4$ kcal/mol). Both the quinoid dimethylene phenanthrene (Equation (13)) and dimethylene biphenyl (Equation (12)) reference molecules have singlet biradical instabilities (see Methods section), but the energy differences between their restricted singlet and unrestricted biradical singlet states are small (*ca.* 2.6 kcal/mol and 1.2 kcal/mol, respectively).

Equation (12)

(Uncorrected value: +34.2 kcal/mol at B3LYP/6-311+G** including ZPE; ASE = +58.3 kcal/mol after two Clar ring and one *avg* mismatch corrections – see text)

Equation (13)

(Uncorrected value: +38.8 kcal/mol at B3LYP/6-311+G** including ZPE; ASE = +66.6 kcal/mol after two Clar and three *avg* mismatch corrections – see text)

As documented above, pyrene, biphenyl, and phenanthrene are all stabilized by aromaticity to a similar extent per π electron. This is shown directly by the homodesmotic disproportionation reaction, Equation (14), which, when evaluated with the experimental heats of formation ($\Delta_f H^\circ_{298}$), is thermoneutral within experimental error ($+1.2 \pm 2.7$ kcal/mol) [19]. Likewise, the corrected ASEs computed for pyrene, phenanthrene and biphenyl also predict essential thermoneutrality (+0.4 kcal/mol). Note also that the wavefunction instability errors of the ASEs of pyrene (4.0 kcal/mol), phenanthrene (2.6 kcal/mol) and biphenyl (1.2

kcal/mol), evaluated based on Equations (11)-(13), largely cancel in Equation (14). Thus, we conclude that the aromaticity of pyrene is not reduced because of its $4n \pi$ electron count.

Equation (14)

($+1.2 \pm 2.7$ kcal/mol; expt. $\Delta_f H^\circ_{298}$; no corrections. Our ASE values give $+0.4$ kcal/mol.)

3.3. Block Localized Wavefunction (BLW) Evaluations. ASEs also can be evaluated computationally by employing the specifically designed BLW [28] method to estimate the PWREs [13] (see Methods section) of the arene as well as the conjugated olefin reference compounds chosen for comparison. This procedure does not employ the total energies of these molecules, but only uses the PWREs to derive “extra cyclic resonance energies” (ECREs). The ECRE measures the greater stabilization associated with the “aromatic” cyclic π electron delocalization of a fully conjugated ring system [37]. ECREs are closely related to ASEs (which are based on evaluations using experimental heats of formation or analogous computed total energies), but have considerable advantages, both conceptually and in practice.

The procedure used to evaluate ECREs largely cancels perturbing energetic effects other than aromaticity, for example ring strain and hybridization imbalance. Thus, the ECRE = 29.3 kcal/mol of benzene, obtained from the energy difference between the PWRE of benzene (61.4 kcal/mol) and that of three *syn* butadienes (PWRE = 10.7 kcal/mol each), is comparable to the ca. 29 kcal/mol ASE values for benzene derived and discussed above (see Equations (4), (5) and (6)). The PWRE for benzene (61.4 kcal/mol) also is close to the experimentally-derived BSRE value (64.6 kcal/mol, see Equation 7). However, this ECRE procedure cannot be applied as straightforwardly to the pyrene ECRE evaluation. Pyrene can be represented by six resonance contributors with one or two Clar rings and different numbers of formal *syn*/anti butadiene moieties (see Figure 1).

Our choice is based on our “avg” procedure (proposed in section 3.2) for correcting the *syn*/anti mismatches of ASE Equations (11)-(13), we first select the resonance contributors with the most Clar rings (e.g. contributors 1–4 for pyrene, Figure 1) and eliminate the rest (e.g. for pyrene, contributors 5 and 6, see Figure 1). For pyrene, each Clar moiety represents three *syn* butadienes. The remaining butadiene moieties of the Kekule structures, which

interact with the top and bottom Clar rings but are neither *syn* nor *anti*, are assigned five *syn/anti* averaged (*avg*) butadiene moieties. Thus, the ECRE of pyrene (74.5 kcal/mol) is given by the energy difference between the PWRE of pyrene (196.2 kcal/mol) relative to the PWRE sum of six *syn* (2 Clar rings, PWRE = 32.1 kcal/mol for each Clar ring) and five *avg* butadienes (*avg* butadiene PWRE = $(10.7 \text{ (syn)} + 12.2 \text{ (anti)})/2 = 11.5$ kcal/mol each). This ECRE value (74.5 kcal/mol) is in excellent agreement with the ASE (74.5 kcal/mol) derived for pyrene from Equation (11). The PWRE value of pyrene given by BLW (196.2 kcal/mol) is of the same magnitude as its BSRE value (218.1 kcal/mol, Equation (8), see section 3.1); both are much larger than the RE given by Jenneskens, et al. [15].

Note that ECREs depend on the formal canonical structure selected for two reasons. First, the BLW energies, computed for various localizations corresponding to the formal structures of individual resonance contributors, differ (as they should). However, these differences, e.g., as shown in Figure 1, are small. Second, the number of *syn-anti* butadiene reference moieties differs for the various canonical forms (as discussed above). Each localization scheme leads to a different ECRE value, but those having the same number of Clar sextet rings give similar values. Specifically, the ECREs based on pairs of equivalent contributors 1, 2 (74.5 kcal/mol) and 3, 4 (75.1 kcal/mol) (both have two Clar sextets) are close in energy. We chose the ECRE of the canonical structure (contributors 1 and 2) with the greatest number of formal *syn* butadiene units, since the PWRE difference between contributors 1–4 are negligible (see Figure 1). In agreement with Bird's comparative evaluation [14] and the VB-based computations of Jenneskens *et al.* [15], the relative importance of contributors 1–4 are greater than contributors 5 and 6.

Based on the same BLW procedure, we computed PWREs of D_{2h} biphenyl (133.0 kcal/mol) [38] and phenanthrene (165.2 kcal/mol). These data are in line with, but smaller than their BSRE values (biphenyl: 141.0 kcal/mol, Equation (10); phenanthrene: 180.2 kcal/mol, Equation (9)). The ECREs of biphenyl (57.3 kcal/mol) and phenanthrene (66.7 kcal/mol), based on their resonance canonical forms with the greatest number of *syn* butadiene units, agree with their *syn-anti* corrected ASE values given by Equations (12) and (13) (see Table 1). Based on the same ECRE procedure applied for pyrene, the ECRE of phenanthrene is derived from the PWRE of phenanthrene relative to the PWRE sum of six *syn* (10.7 kcal/mol each) and three *avg* (11.5 kcal/mol each) butadienes. The ECRE of biphenyl is derived from the PWRE difference between biphenyl and the sum of six *syn* and one *avg* butadiene. The ECREs per ring carbon of biphenyl (4.8 kcal/mol), phenanthrene (4.8 kcal/mol) and pyrene (4.7 kcal/mol) are almost the same as that of benzene (4.9 kcal/mol) (see

Table 1). Although stabilized by aromaticity to a similar extent, the overall PWRE, per ring carbon, of pyrene, phenanthrene, biphenyl and benzene, decreases in the following order: pyrene (12.3 kcal/mol) > phenanthrene (11.8 kcal/mol) > biphenyl (11.1 kcal/mol) > benzene (10.2 kcal/mol). Note that PWREs measure the total stabilization of a molecule, which includes interactions not evaluated in ECRE estimates. Biphenyl is a good example, since its PWRE (but not the ECRE) includes the non-Clar conjugation (*ca.* 11 kcal/mol, similar to that of butadiene) between the two Clar rings. Thus, the PWRE of biphenyl is more than twice that of benzene (see Table 1). Likewise, the PWREs of phenanthrene and pyrene also include non-Clar conjugative interactions.

4. Conclusion

Isodesmic or homodesmotic equations employed for aromatic stabilization energy (ASE) and resonance energy (RE) evaluations for polycyclic arenes are difficult to devise to isolate the desired energetic effects as the reference molecules often are complicated by other perturbing influences. However, isodesmic bond separation resonance energy (BSRE) evaluations of strain-free arenes are non-arbitrary, well-defined, use simple reference molecules for which experimental data are available, and the drawback of inherent hybridization imbalance may largely be compensated. The BLW method provides a general, direct approach for evaluating Pauling–Wheland REs, as no additional reference compounds, other than the system itself, is needed.

ASE evaluations are inherently more complex as they require comparisons with conjugated, but non-aromatic reference systems, which seldom are free from other complicating energetic effects. ASE evaluations of unstrained arenes may employ butadiene as the smallest π conjugated reference model. However, *syn*-butadiene, rather than its 3.7 kcal/mol more stable *anti*-butadiene isomer, represents the predominant conformation in arenes. Thus, benzene requires three *syn*-butadiene models. Polycyclic aromatics incorporate *syn*- but also *avg* (averaged) butadiene moieties. The extra cyclic resonance energies (ECREs, akin to ASEs) can also be derived by comparing the BLW computed PWRE of the aromatic molecule with the PWRE of the chosen reference system. Other energetic effects do not perturb such comparison.

Based on both ASE and ECRE evaluations, the aromatic stabilization per ring carbon of biphenyl, phenanthrene, pyrene, and benzene are all nearly the same. Hence, the aromaticity of pyrene is not diminished because of its $4n$ π electron count. In contrast, both the PWRE and the BSRE values *per carbon* increase in going from benzene to biphenyl, due

to the extra conjugation between the two phenyl rings. Phenanthrene and especially pyrene benefit even more from such extra non-Clar conjugation. These non-Clar conjugations are not taken into account in the ECRE and ASE estimates, but are included when evaluating the total stabilization of molecules, based on their PWREs and BSREs.

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- [20] For example, NIST gives both 26.00 ± 0.19 kcal/mol and 26.75 ± 0.23 kcal/mol for the $\Delta_f H^\circ_{298}$ of butadiene, but provides no basis for selecting one over the other. Since butadiene is used 11 times in Equations (1) and (2), this 0.75 kcal/mol difference (and the associated error bars) results in experimental uncertainties well over 10 kcal/mol! The earlier “selected value” for butadiene of Cox and Pilcher [34b] is 26.11 ± 0.15 kcal/mol. Schaefer, Allen, et. al. have overcome this difficulty by high level theoretical focal-point analysis methods, which computes gas phase $\Delta_f H^\circ$ values to ca. ± 0.2 kcal/mol accuracy [21]. This method, which, systematically incorporates very high level electron correlation and extrapolates ab initio energies to the complete basis set limit, also favors the lower value for butadiene [21f] given in NIST. Hence, we have employed $\Delta_f H^\circ_{298} = 26.00 \pm 0.19$ kcal/mol for butadiene in Equations 1 and 2.
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- [33] A referee has noted that the heat of formation per carbon for pyrene ($53.94/16 = 3.37$ kcal/mol) [19] also is essentially the same as benzene ($19.82/6 = 3.30$ kcal/mol) [19].

But since pyrene, with 10 CH's and 6 C's, has different groups from benzene (6 CH's), this has little relevance in the ASE context. We note that the heat of formation per carbon of the non-aromatic diamond is nearly the same as that for the highly aromatic graphite.

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Figure 1. BLW computed PWREs and ECREs (at B3LYP/6-31G*) of different pyrene resonance contributors. The formal number of *syn* and *anti* butadiene moieties of each contributor (1-6) are given below each structure. The PWREs are computed directly, but the ECREs of each of the resonance contributors are derived from the PWRE of the resonance contributor itself relative to the sum of the PWREs of the assigned number of Clar and type of butadiene references that represents the specific resonance contributor ($10.7 \times 3 = 32.1$ kcal/mol for each Clar ring and 11.5 kcal/mol for each *syn/anti* averaged butadiene). For example, the ECRE of Contributor 1 and 2 is $196.2 - (2 \times 32.1 + 5 \times 11.5) = 74.5$ kcal/mol.

	1	2	3
Total energy of closed shell singlet including ZPE (Hartrees)	-693.03269	-693.02335	-693.01290
Total energy of biradical including ZPE (Hartrees)	-693.03913	-693.03717	-693.03653
$\langle S \rangle$	0.79	1.02	1.10
Relative energy of closed vs. open shell singlet (kcal/mol)	4.0	8.7	14.8
Polarization Energy (kcal/mol)	0.0	0.0	0.1
ASE based on Equation (11) including ZPE (kcal/mol)	43.0	48.9	55.4
Total number of articulatedene subunits	12	9	6
Number of syn-anti correction (g / kcal/mol each)	8.5	5.5	2.5
ASE after syn-anti correction (kcal/mol)	74.5	69.3	64.7

Figure 2. Dihydrodimethylene-substituted dihydroquinoidalpyrene references (**1**, **2** and **3**) employed in Equation (11) for the pyrene ASE evaluation. The ASE values presented in row six are uncorrected. Row nine presents the ASE value after appropriate syn-anti butadiene mismatch correction (the number of corrections applied are indicated in row eight). All data were computed at the B3LYP/6-311+G** level including ZPE.

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Table 1. ASE (corrected for syn-anti butadiene mismatches, based on the appropriate homodesmotic equations evaluated at the B3LYP/6-311+G** level, see text), ECRE (BLW), PWRE (BLW) and experimental BSRE values of pyrene, phenanthrene, biphenyl and benzene. All BLW data were computed at the B3LYP/6-31G* level.

	Pyrene	Phenanthrene	Biphenyl (D_{2h})	Benzene
ASE (kcal/mol)	74.5	66.6	58.3	29.3
ASE per ring carbon (kcal/mol)	4.7	4.8	4.9	4.9
ECRE (kcal/mol)	74.5	66.7	57.3	29.3
ECRE per ring carbon (kcal/mol)	4.7	4.8	4.8	4.9
PWRE (kcal/mol)	196.2	165.2	133.0	61.4
PWRE per ring carbon (kcal/mol)	12.3	11.8	11.1	10.2
BSRE (kcal/mol)	218.1	180.2	141.0	64.6
BSRE per ring (kcal/mol)	13.6	12.9	11.8	10.8