

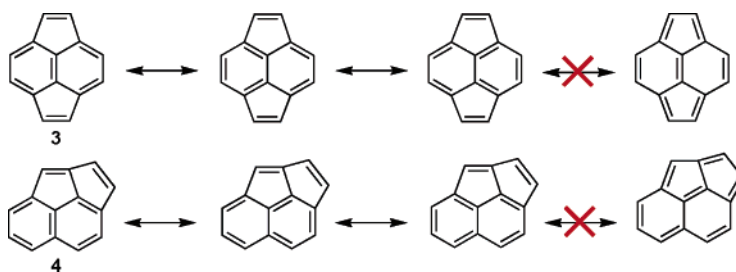
## An ab Initio Valence Bond Study on Cyclopenta-Fused Naphthalenes and Fluoranthenes

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To probe the effect of external cyclopenta-fusion on a naphthalene core, ab initio valence bond (VB) calculations have been performed, using strictly atomic benzene p-orbitals and p-orbitals that are allowed to delocalize, on naphthalene (1), acenaphthylene (2), pyracylene (3), cyclopenta[*b,c*]-acenaphthylene (4), fluoranthene (5), and cyclopenta[*c,d*]fluoranthene (6). For the related compounds 1–4 and 5,6 the total resonance energies (according to Pauling's definition) are similar. Partitioning of the total resonance energy in contributions from the possible  $4n + 2$  and  $4n$   $\pi$ -electron conjugated circuits shows that only the  $6\pi$ -electron conjugated circuits (benzene-like) contribute to the resonance energy. The results show that cyclopenta-fusion does not extend the  $\pi$  system in the ground state; the five-membered rings act as *peri*-substituents. As a consequence, the differences in (total) resonance energy do not coincide with the differences in thermodynamic stability. Notwithstanding, the relative energies of the Kekulé structures can be estimated using Randić's conjugated circuits model.

### Introduction

The chemical and physical properties of mono- and polycyclic  $\pi$ -conjugated systems are frequently rationalized in terms of their aromatic character. Unfortunately, however, aromaticity is not clearly defined.<sup>1–5</sup> Various criteria exist, e.g. the geometry,<sup>3</sup> energy, magnetic properties,<sup>1,6</sup> and chemical reactivity.<sup>7</sup> Furthermore, different

empirical models, such as Clar's model of the aromatic sextet<sup>8</sup> and Randić's  $\pi$ -electron conjugated circuits model,<sup>9–12</sup> are also applied to rationalize the physico-chemical properties of extended  $\pi$ -conjugated polycyclic aromatic hydrocarbons. The energetic criterion that follows the original proposal by Pauling<sup>13,14</sup> comprises the resonance energy ( $E_{\text{res}}$ ) and the contributions of the possible Lewis structures to the wave function. The importance of the various Kekulé resonance structures can be reliably assessed using ab initio valence bond (VB) theory.

We have recently shown using ab initio VBCI<sup>15</sup> and magnetic property calculations (exaltation of the mag-

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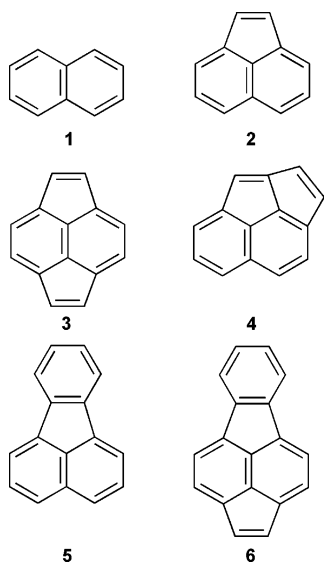
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## SCHEME 1



netizability, NICS,<sup>16</sup> explicit ring-current mapping<sup>17</sup>) on all cyclopenta-fused pyrene congeners that (multiple) cyclopenta-fusion does not affect the VB resonance energy but does influence the magnetic properties. An important outcome was that the total resonance energy ( $E_{\text{res}}$ ) does not correlate with the relative total energies ( $E_{\text{tot}}$ ) of isomers in a particular series. Thus, aromatic character according to the  $E_{\text{res}}$  criterion does not follow thermodynamic stability.<sup>16,18</sup> A corollary is that upon cyclopenta-fusion the effect of the  $\sigma$  skeleton should be taken into account. The ab initio VBCI results obtained for the cyclopenta-fused pyrene series<sup>15</sup> raise several questions: (1) Is the behavior of the cyclopenta-fused pyrene congeners an exception, or is there in general no correlation between the thermodynamic stability of isomers of CP-PAHs and the differences in their resonance energies? (2) To what extent does cyclopenta-fusion exert an effect on the resonance energy ( $E_{\text{res}}$ ) of a PAH? (3) To what extent does the Lewis-structure description relate to its magnetic properties? To obtain answers to these questions we have performed an ab initio VBCI and VBSCF study on the cyclopenta-fused naphthalene derivatives **1–6** (Scheme 1).

Not all of the molecules **1–6** have been synthesized yet. Hitherto cyclopenta[*b,c*]acenaphthylene (**4**) has only been put forward as a transient intermediate in high-temperature gas-phase reactions.<sup>19,20</sup> Although **1–6** all possess a naphthalene core, their behavior<sup>21</sup> and espe-

cially their magnetic properties were found to be quite different.<sup>6,21–24</sup> For example, it has been shown that the annelation of two pentagons to a naphthalene core, giving pyracylene (**3**), results in intense paratropic currents in the pentagons, while the diatropic current within the naphthalene-unit persists but weakens.<sup>23</sup> This is substantiated by a decrease of NICS<sup>6</sup> value in the center of the hexagons of the naphthalene ring.<sup>6,25</sup> Only for **4**, the diatropic naphthalene-like ring current breaks down and is replaced by a current that becomes concentrated in one of the hexagons.<sup>24</sup> On the basis of the computed ring current maps of **4**, it has been concluded that **4** resembles an “annelated pentalene”. The NICS (0 Å) data of **4** also supports this interpretation: the NICS(0) for the hexagon that is adjacent to both pentagons is  $-12.3$  ppm, whereas that of the other hexagon is only  $-6.7$  ppm.

**Valence Bond Description.** The advantage of VB theory is that it will reveal changes in the electronic structure of the naphthalene core in a pictorial sense, i.e., it gives insight how the contributions of the different Kekulé resonance structures will change upon (progressive) cyclopenta-fusion and its topology. Since the aromatic character of PAHs **1–6** will be assessed using the energetic criterion, the results will reveal whether the origin of the differences in chemical behavior lies in the differences in the  $\pi$ -systems.

Besides insight in the different weights of the Kekulé resonance structures, ab initio VB theory can also be used to calculate the energy gain [resonance energy ( $E_{\text{res}}$ )] due to resonance between Lewis structures.<sup>13,14</sup> Furthermore,  $E_{\text{res}}$  can be decomposed into contributions from “electron delocalization” in various distinct  $4n + 2$  and  $4n$   $\pi$ -electron conjugated circuits.<sup>15</sup>

In VB theory, a bond is made by the coupling of the spin of two electrons in two (singly occupied) orbitals into a singlet. The atomic orbitals can be chosen either to be fixed and strictly centered on one atom (strictly atomic model) or may be optimized without constraints (cf. ref 26) and thus are allowed to delocalize (delocal model). Using these two approaches, the energy of each particular Kekulé resonance structure is computationally accessible. The total wave function is then written as a linear combination of the chosen set of structures. As a consequence of the resonance between the contributing structures, the total energy ( $E_{\text{tot}}$ ) will be lowered with respect to the energy of each individual structure. According to Pauling,<sup>13,14</sup> the energy gain that results from resonance with respect to the most stable Kekulé-type resonance structure represents the resonance energy ( $E_{\text{res}}$ ). In our previous paper on the cyclopenta-fused pyrene congeners,<sup>15</sup> use was made only of strictly atomic p-orbitals (VBCI), which were optimized for benzene, to describe the  $\pi$ -electron conjugated system. The recent advance in computer technology enables valence bond calculations with p-orbitals, which are completely optimized and are

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allowed to delocalize (VBSCF, delocal model) for compounds of the size of **1–4**. Hence, the applicability of our initial constraint of fixed, strictly atomic p-orbitals can be validated, and the effect of optimization of the p-orbitals can be assessed by a comparison of the strictly atomic VB results for **1–4** with those obtained by calculations using the delocal model.

Earlier ab initio VB calculations on naphthalene (**1**), using the spin-coupled approach,<sup>27</sup> which is similar to the delocal model, showed that only the three Kekulé-type resonance structures contribute. Hence, in our ab initio VBCI and VBSCF calculations for **1–6**, we include only the Kekulé-type resonance structures. Note that the exclusion of ionic and Dewar-like resonance structures facilitates the interpretation of the wave function.

## Computational Details

**Geometries.** For consistency with our previous results on all cyclopenta-fused pyrene congeners,<sup>15</sup> we have optimized the geometries of **1–6** at the RHF/6-31G level of theory using GAMESS-UK<sup>28</sup> (see Supporting Information for Cartesian coordinates). Note that these geometries were found to be in good agreement with RHF/6-31G\*\* and B3LYP/6-31G\*\* optimized geometries.<sup>23,24</sup> All stationary states correspond to genuine minima according to Hessian calculations.

**Valence Bond Calculations.** The ab initio VB calculations were performed with the TURTLE<sup>29,30</sup> program package as now implemented in GAMESS-UK.<sup>28</sup> The VB wave functions were constructed from all possible Kekulé-type resonance structures (Scheme 2). Weights ( $W$ ) to each structure  $i$  in the wave function can be assigned according to the formula  $W_i = \sum_j c_j c_j S_{ij}$  derived by Chirgwin and Coulson,<sup>31</sup> in which  $c_i$  represents the variationally determined coefficient of structure  $i$ , and  $S_{ij}$  is the overlap between structures  $i$  and  $j$ . The  $\pi$ -system in the VBCI calculations was described by strictly atomic non-orthogonal p-orbitals, optimized for benzene.<sup>15</sup> The applicability of benzene p-orbitals for the description of  $\pi$ -systems of PAHs was verified in our previous study of the cyclopenta-fused pyrene congeners with restricted orbital optimization.<sup>15</sup> The recent development of a parallel version of the valence bond program TURTLE<sup>32</sup> in combination with the steady increase of computer power enables the VBSCF calculations of compounds of the size of **1–4**. Here, the VBSCF results, where the p-orbitals are fully optimized, are compared to those obtained using the strictly atomic model for further justification of the latter method. Unfortunately, similar VBSCF calculations on **5** and **6** are still computationally too demanding. In all VB calculations, the  $\sigma$  cores were taken from preceding RHF/6-31G calculations.

**Partitioning of the Resonance Energy ( $E_{\text{res}}$ ).** The total resonance energy ( $E_{\text{res}}$ ) can be partitioned in resonance

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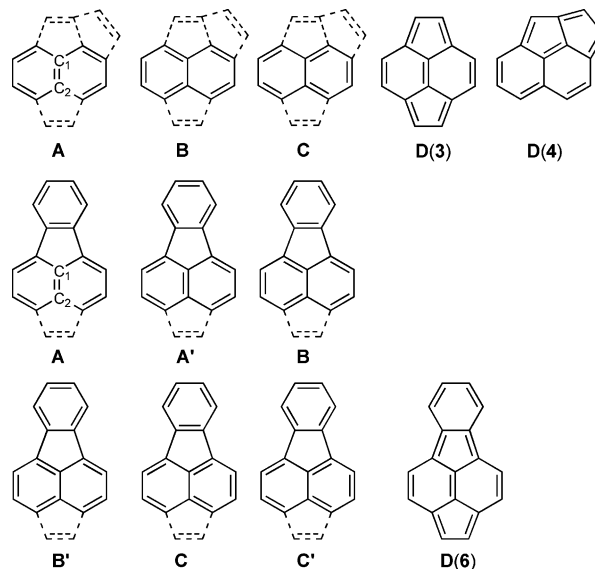
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## SCHEME 2. Kekulé Resonance Structures Considered in the VB Calculations for **1–6** (cf. Tables 1 and 2)



**TABLE 1. Total Energies (RHF/6-31G and VBCI/6-31G) of **1–6** (in  $E_h$ ) and Their Resonance Energies  $E_{\text{res}}$  and  $E_{\text{res}}^m$  (in kJ/mol)<sup>a</sup>**

compd <sup>b</sup>	RHF	VB	$E_{\text{res}}$	$E_{\text{res}}^m$
<b>1</b> (3)	-383.222722	-383.070533 <i>-383.336648</i>	-133.2 <i>-56.1</i>	-268.5 <i>-403.5</i>
<b>2</b> (3)	-458.911067	-458.727786 <i>-459.051142</i>	-121.4 <i>-49.8</i>	-268.2 <i>-404.4</i>
<b>3</b> (4)	-534.574673	-534.368581 <i>-534.745179</i>	-112.6 <i>-44.4</i>	-275.1 <i>-413.0</i>
<b>4</b> (4)	-534.541544	-534.336739 <i>-534.712694</i>	-126.4 <i>-49.0</i>	-277.4 <i>-413.5</i>
<b>4-H<sub>2</sub></b> (3) <sup>c</sup>	-458.830890	-458.646587	-120.6	-268.4
<b>5</b> (6)	-611.531888	-611.268190	-223.8	-449.4
<b>6</b> (7)	-687.199857	-686.909709	-205.4	-451.7
benzene (2)	-230.624474	-230.540386 <i>-230.692579</i>	-116.1 <i>-83.6</i>	-184.5 <i>-254.0</i>

<sup>a</sup> The VBSCF/6-31G results are reported in italics. <sup>b</sup> The number of Kekulé structures is given between parentheses. <sup>c</sup> Acenaphthylene (**2**) in the geometry of **4** (see text).

contributions of particular  $\pi$ -electron conjugated circuits.<sup>15</sup> Therefore, the  $\mathbf{H}$  matrix is transformed to an orthogonal structure basis (Löwdin orthogonalization<sup>33</sup>), so that the total energy ( $E_{\text{tot}}$ ) can be written as a sum of the diagonal elements ( $H_{ii}$ ) and off-diagonal elements ( $H_{ij}$ ) ( $E_{\text{tot}} = \sum_i c_i^2 H_{ii}^{\perp} + 2\sum_{i<j} c_i c_j H_{ij}^{\perp}$ ). The sum of the off-diagonal elements represents the resonance energy with respect to the mean energy of the different Kekulé structures ( $E_{\text{res}}^m$ ). Each resonance interaction between two structures  $i$  and  $j$  leads to one particular  $\pi$ -electron conjugated circuit, and the off-diagonal element between structures  $i$  and  $j$  ( $2c_i c_j H_{ij}^{\perp}$ ) can be defined as the contribution to  $E_{\text{res}}^m$  as a result of this resonance. Note that  $E_{\text{res}}^m$  is not equal to  $E_{\text{res}}$ .

## Results and Discussion

**Resonance Energies.** In Table 1, the total energies ( $E_{\text{tot}}$ ) calculated at the RHF/6-31G and VB/6-31G levels of theory are presented, together with the derived VB resonance energies  $E_{\text{res}}$  and  $E_{\text{res}}^m$ . A survey of the reso-

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**TABLE 2.** Weights of Kekulé-Type Resonance Structures of 1–4 and 5,6 (Scheme 2)<sup>a</sup>

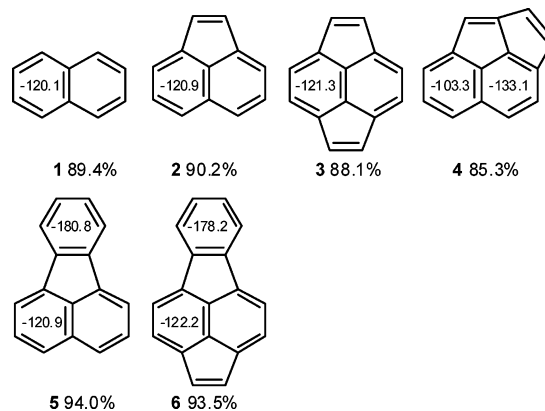
compd	A	A'	B	B'	C	C'	D(n) <sup>b</sup>
1	0.473 (0.0)		0.264 (74.9)		0.264 (74.9)		
2	0.505 (0.0)		0.247 (99.1)		0.247 (99.1)		
3	0.537 (0.0)		0.228 (126.1)		0.228 (126.1)		0.007 (408.2)
4	0.489 (0.0)		0.192 (132.2)		0.304 (65.3)		0.015 (362.5)
4-H <sub>2</sub> <sup>c</sup>	0.508 (0.0)		0.202 (129.9)		0.289 (79.4)		
5	0.222 (32.1)	0.275 (0.0)	0.110 (130.2)	0.142 (89.3)	0.110 (130.2)	0.142 (89.3)	
6	0.217 (54.8)	0.309 (0.0)	0.094 (177.1)	0.141 (112.8)	0.094 (177.1)	0.141 (112.8)	0.004 (397.0)

<sup>a</sup> Relative energies (in kJ/mol) appear in parentheses. <sup>b</sup> *n* is the compound number (see also Scheme 1). <sup>c</sup> Acenaphthylene (**2**) in the geometry of **4** (see text).

nance energy ( $E_{\text{res}}$ ) values shows that these are of similar magnitude for series 1–4 and 5,6. This strongly suggests that cyclopenta-fusion only exerts a minor effect on the total resonance energies of the cyclopenta-fused naphthalenes 1–4 and fluoranthenes 5,6. Similar results were found for the cyclopenta-fused pyrene series.<sup>15</sup> Note that the resonance energies obtained using the strictly atomic orbital model will be overestimated. This is due to a less favorable description of the double bonds in the individual resonance structures (see “The Influence of the Valence Bond Model”).

Further support for the minor influence of cyclopenta-fusion on the resonance energy ( $E_{\text{res}}$ ) is given by a survey of the relative energies of the contributing Kekulé resonance structures and their weights (Table 2). The data show that for 1–4 the most important contributing Kekulé resonance structure is that with the maximum number of 6 $\pi$ -electron conjugated circuits (benzene-like), viz., the Fries<sup>34</sup> structure **A** (Scheme 2). Upon progressive cyclopenta-fusion in going from **1** to **2** and finally to **3** or **4**, the weight of structure **A** increases. The energy of the structures **B** and **C** increases relative to that of **A**. For **3** and **4**, the fourth possible Kekulé resonance structures with only 4*n*  $\pi$ -electron conjugated circuits (structures **D**(**3**) and **D**(**4**), respectively, Scheme 2; see also ref 12) possess a very high energy in comparison to the related most stable structure **A**. In addition, they have negligible weights in their wave functions. Interestingly, in **4**, the unsymmetrical substitution pattern clearly influences the relative weights and energies of the Kekulé structures **B** and **C**. Structure **C**, favoring the radialene fragment, is lower in energy and more important in the VB wave function than structure **B** (Table 2, Scheme 2), in which a pentalene substructure is present.

To distinguish between electronic and/or structural effects due to the addition of a second five-membered ring in the case of **4**, an ab initio VBCI calculation was performed on **2** but fixed in the geometry of **4** (denoted by 4-H<sub>2</sub>). For 4-H<sub>2</sub>, the relative energies and the structure weights of the structures **B** and **C** are similar to those found in **4** (Tables 1 and 2). This indicates that the dominant effect of adding the second five-membered ring

**SCHEME 3.** Kekulé Structures of 1–6 and Contribution of the 6 $\pi$ -Electron Conjugated Circuits (Benzene-Like) (in kJ/mol) and Their Relative Contribution to the Total Mean Resonance Energy ( $E_{\text{res}}^{\text{m}}$ ), As Calculated Using the Strictly Atomic Model

in the case of **4** on the different contributions from the structures **B** and **C** is caused by strain imposed by the  $\sigma$ -skeleton.

Although **4** is 87.0 kJ/mol [ $\Delta E_{\text{tot}}(\text{RHF}/6\text{-}31\text{G})$ ] less stable than **3**, the difference in resonance energy [ $\Delta E_{\text{res}} = E_{\text{res}}(\mathbf{3}) - E_{\text{res}}(\mathbf{4})$ ] is only 13.9 kJ/mol. Hence, for isomers **3** and **4** the  $\pi$ -electron resonance is only marginally influenced by the cyclopenta-fusion topology. Notwithstanding, the mode of cyclopenta-fusion markedly affects the imposed strain on the  $\sigma$ -skeleton as reflected by the substantial difference between their  $E_{\text{tot}}$  values. In general, a high thermodynamic stability does not follow from a high resonance energy ( $E_{\text{res}}$ ).<sup>15,18</sup>

The partitioning of the resonance energy ( $E_{\text{res}}^{\text{m}}$ ) in contributions from the different contributing  $\pi$ -electron conjugated circuits in 1–4 shows that the 6 $\pi$ -electron conjugated circuits have the largest contribution to the resonance energy ( $E_{\text{res}}$ ). In Scheme 3, the contributions of the distinct 6 $\pi$ -electron conjugated circuits (benzene-like) are indicated, together with their total contribution to the mean resonance energy ( $E_{\text{res}}^{\text{m}}$ ). For 1–3, both six-membered rings are symmetrically equivalent and will have the same contribution to the total resonance energy ( $E_{\text{res}}$ ). In **4**, the right six-membered ring is more aromatic than the left one. For 1–4, the contributions of the resonances in the six-membered rings dominate the total resonance energy (more than 85%, Scheme 3), which is in agreement with a Clar description.<sup>8</sup> Other 4*n* + 2 (*n* = 2, 3, ...) and 4*m* (*m* = 1, 2, ...)  $\pi$ -electron conjugated circuits contribute less than 15% to the total mean resonance energy.

The trend, that upon cyclopenta-fusion structure **A** becomes more important in the total wave function, is also in line with the changes in the bond length C(1)–C(2) (Scheme 2 and Supporting Information); the C(1)–C(2) bond length decreases (**1**, 1.413 Å; **2**, 1.380 Å; **3**, 1.338 Å) upon cyclopenta-fusion.

The available ring current maps<sup>23</sup> for 1–3 show that the  $\pi$ -ring current is a superposition of a diatropic, naphthalene-like current, and a paratropic current in the pentagons. In the case of **4**, a stronger benzene-like current is found in the hexagon that has the highest contribution to the total resonance energy.<sup>24</sup>

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For fluoranthene (**5**) and cyclopenta[*c,d*]fluoranthene (**6**) also the structure with the lowest number of double bonds within the five-membered rings and the maximum number of  $6\pi$ -electron conjugated circuits is the most stable one (**A'**, Scheme 2 and Table 2). In analogy to the trends seen in the series **1–4** the energies of the distinct Kekulé structures are raised with respect to the most stable one with the increasing number of double bonds in the five-membered rings. Note that the “anti-aromatic” (anti-Fries<sup>35</sup>) Kekulé structure **D(6)**, which possesses only  $4n$   $\pi$ -electron conjugated circuits,<sup>12</sup> does not contribute to the wave function of **6**. The  $6\pi$ -electron conjugated circuit resonance interactions (**A**  $\leftrightarrow$  **A'**, **B**  $\leftrightarrow$  **B'**, and **C**  $\leftrightarrow$  **C'**) in the top six-membered rings have the highest contribution to  $E_{\text{res}}^{\text{m}}$ , which is close to the benzene value ( $E_{\text{res}}^{\text{m}} = -184.8$  kJ/mol).<sup>15</sup> The resonance interactions, leading to the  $6\pi$ -electron conjugated circuits within the naphthalene substructure, between **A'**  $\leftrightarrow$  **B'**, **A'**  $\leftrightarrow$  **C'**, **A**  $\leftrightarrow$  **B**, and **A**  $\leftrightarrow$  **C** follow in importance. These resonance interactions within the  $6\pi$ -electron conjugated circuits comprise more than 93% of the total resonance energy (Scheme 3). Other resonance interactions between structures that lead to  $\pi$ -electron conjugated circuits with more than  $6\pi$ -electrons do not contribute, in line with the trends found in our previous ab initio VBCI calculations on the cyclopenta-fused pyrenes.<sup>15</sup> In agreement with the results obtained for **1–4** the bond length changes in the C(1)–C(2) bonds (Scheme 2 and Supporting Information) are accompanied by an increase in weights of the Kekulé structures **A** and **A'** [C(1)–C(2): **5**, 1.385 Å; **6**, 1.342 Å].

The sum of the resonance energies of benzene and naphthalene (**1**) and benzene and acenaphthylene (**2**) show reasonable agreement with the total resonance energies (both  $E_{\text{res}}$  and  $E_{\text{res}}^{\text{m}}$ ) directly computed for **5** [ $E_{\text{res}}(\text{benzene}) + E_{\text{res}}(\mathbf{1}) = -249.3$  kJ/mol;  $E_{\text{res}}^{\text{m}}(\text{benzene}) + E_{\text{res}}^{\text{m}}(\mathbf{1}) = -453.0$  kJ/mol; Table 1] and **6** [ $E_{\text{res}}(\text{benzene}) + E_{\text{res}}(\mathbf{2}) = -237.5$  kJ/mol;  $E_{\text{res}}^{\text{m}}(\text{benzene}) + E_{\text{res}}^{\text{m}}(\mathbf{2}) = -452.7$  kJ/mol; Table 1], respectively. This shows that, in line with Clar’s description of PAHs,<sup>8</sup> the interaction between the benzene ring and the naphthalene core in the case of both **5** and **6** is small. This disjoint character is also visible in the  $\pi$ -ring current maps and other integrated magnetic properties derived thereof of **5** and **6**.<sup>23</sup>

**Influence of the Valence Bond Model.** As discussed in the computational section, the applicability of the strictly atomic orbital model is verified by performing ab initio VBSCF calculations for **1–4**, in which the p-orbitals on each carbon were fully optimized (delocal model; Tables 1 and 3). The delocal model gives similar trends in weights of structures and resonance energies, compared to those obtained using strictly atomic p-orbitals, optimized for benzene (Tables 1 and 2).

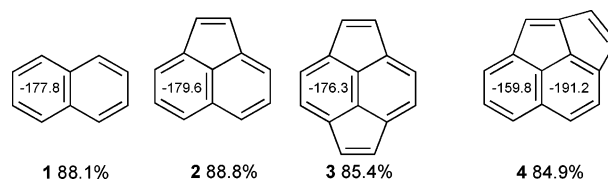
A similar analysis of the resonance energy ( $E_{\text{res}}$ ) in contributions of  $\pi$ -electron conjugated circuits as made for the local model is presented in Scheme 4. The differences between the strictly atomic orbital model and VBSCF model are only in the absolute values of the contributions to  $E_{\text{res}}^{\text{m}}$ ; the fractional contribution of the resonances in the  $6\pi$ -electron conjugated circuits does not

**TABLE 3.** Weights of Kekulé-Type Resonance Structures of **1–4** (Scheme 3) As Calculated Using the VBSCF Delocal Orbital Model<sup>a</sup>

compd	A	B	C	D( <i>n</i> ) <sup>b</sup>
<b>1</b>	0.583 (0.0)	0.209 (180.0)	0.209 (180.0)	
<b>2</b>	0.614 (0.0)	0.193 (199.8)	0.193 (199.8)	
<b>3</b>	0.642 (0.0)	0.175 (220.1)	0.175 (220.1)	0.008 (701.1)
<b>4</b>	0.620 (0.0)	0.145 (244.3)	0.227 (169.9)	0.008 (659.2)

<sup>a</sup> Relative energies (in kJ/mol) appear in parentheses. <sup>b</sup> *n* is the compound number (see also Scheme 1).

**SCHEME 4.** Kekulé Structures of **1–4** and Contribution of the  $6\pi$ -Electron (Benzene-Like) Conjugated Circuits (in kJ/mol) and Their Relative Contribution to the Total Mean Resonance Energy ( $E_{\text{res}}^{\text{m}}$ ), As Calculated Using the VBSCF Delocal Model



change, and these resonance interactions still remain the main contributors to the total resonance energy.

The VBSCF results of **1** are in agreement with those previously reported using the spin-coupled VB method<sup>27</sup> (weight of structure **A** 0.504;  $E_{\text{res}} -71.0$  kJ/mol). The small difference between the latter  $E_{\text{res}}$  value and that found by us in the delocal approach ( $E_{\text{res}} -56.1$  kJ/mol, Table 3) is attributed to the difference in basis set.

The difference in resonance energy ( $E_{\text{res}}$ ) of the delocal VBSCF calculations compared to that of the strictly atomic orbital model ( $E_{\text{res}} -133.2$  kJ/mol, Table 1) is explained by the fact that strictly atomic p-orbitals lead to a less favorable description of the double bonds in the individual resonance structures. As a consequence, the effect of resonance will be overestimated, although conclusions with regard to which resonances in PAHs are important remain unaffected.

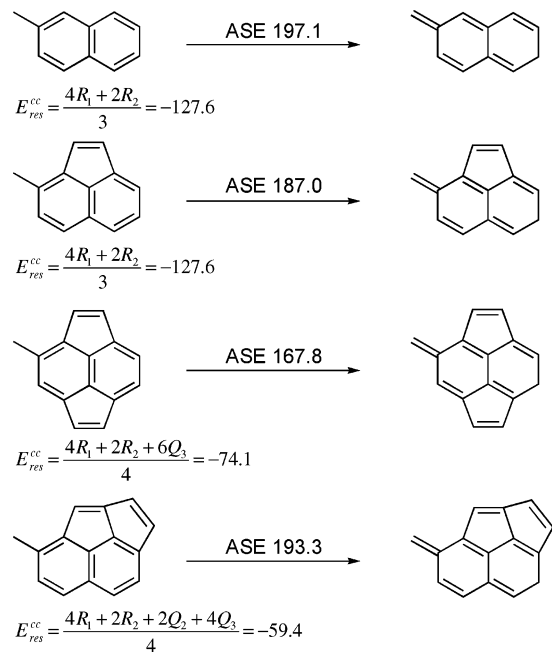
**Resonance Energy, Aromatic Stabilization Energy, Conjugated Circuits Resonance Energy, and the Experimental Enthalpy of Hydrogenation.** The outcome of our ab initio VBCI and VBSCF calculations that the  $E_{\text{res}}$  values of **1–4** and **5,6** are nearly identical is further substantiated by independently computed aromatic stabilization energies (ASEs)<sup>36,37</sup> of **1–4**. In these calculations the ASE in its simplest form is defined as the energy difference between the methyl-substituted derivative and the quinoid derivative, as shown in Scheme 5. This isodesmic isomerization energy between two closely related compounds with a similar strain content provides an estimate of the  $\pi$ -electron resonance energy in line with the ab initio VB  $E_{\text{res}}$  values. Besides the ASE values, resonance energies calculated using

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**SCHEME 5. Isodesmotic Reactions for Computing the Aromatic Stabilization Energy (ASE)<sup>36,37</sup> (in kJ/mol) and the Resonance Energy of the Aromatic Hydrocarbon According to the  $\pi$ -Electron Conjugated Circuits Model ( $E_{\text{res}}^{\text{cc}}$  in kJ/mol)<sup>a</sup>**



<sup>a</sup> The  $E_{\text{res}}^{\text{cc}}$  values of  $R_n$  ( $4n + 2$ ) and  $Q_n$  ( $4n$ ) were taken from ref 10 (stabilization is denoted by a negative contribution to the resonance energy;  $R_1$  -83.9,  $R_2$  -23.7, and  $R_3$  -9.7 kJ/mol;  $Q_1$  154.4,  $Q_2$  43.4, and  $Q_3$  14.5 kJ/mol).

Randić's  $\pi$ -electron conjugated circuits model ( $E_{\text{res}}^{\text{cc}}$ )<sup>9,10,38</sup> are also indicated next to the ab initio VB  $E_{\text{res}}$  results.

The ASEs of 1–4 decrease only moderately upon progressive cyclopenta-fusion, and the changes are in line with the ab initio VB  $E_{\text{res}}$  results (Table 1). This decrease indicates that cyclopenta-fusion has a small destabilizing effect on the  $\pi$ -system of all cyclopenta-fused derivatives. In marked contrast, the resonance energies calculated using the  $\pi$ -electron conjugated circuits model ( $E_{\text{res}}^{\text{cc}}$ ) show a sudden and significant decrease when two five-membered rings are present in the molecule.<sup>38</sup> A similar behavior was found for the cyclopenta-fused pyrenes.<sup>15,16</sup> However, this trend is not reproduced either by the ab initio VB resonance energies ( $E_{\text{res}}$ ) or by the ASEs.

In the  $\pi$ -electron conjugated circuits model each structure is given an equal weight in the total wave function. However, as our VB calculations revealed, structures with a higher energy contribute considerably less to the wave function (i.e., have a lower weight) and do not influence the resonance energy, in agreement with the variational principle. The relative energies of the VB structures can be estimated with Randić's  $\pi$ -electron conjugated circuits model.<sup>9–12</sup> This is exemplified for 4: the relative energy ordering of the structures (in increasing order) is **A** < **C** < **B** < **D** (Scheme 2, Table 2), and their contributions to the  $\pi$ -electron conjugated circuits resonance energy is  $2R_1 + Q_3$  (**A**) <  $R_1 + R_2 + Q_3$  (**C**) <

$R_1 + R_2 + Q_2$  (**B**) <  $Q_2 + 2Q_3$  (**D**). From this, we can make an estimate of the relative importance of the different structures in the VB wave function and of the resonance energy.

Other criteria for deducing the interaction between the cyclopenteno-bridges and the naphthalene core of 2 and 3 are the available experimental enthalpies of hydrogenation [ $\Delta H_{\text{hyd}}$ (2) = -107.9 kJ/mol;  $\Delta H_{\text{hyd}}$ (3) = -236.0 kJ/mol].<sup>39</sup> These results confirm, in line with our VB results, that there is no significant aromatic interaction between the cyclopenteno-bridges of 2 and 3 and the naphthalene core. A detailed analysis of the redox potentials and in particular their reductive behavior of cyclopenta-fused aromatic hydrocarbons<sup>40</sup> led to the same conclusions.

## Conclusions

Ab initio VBCI and VBSCF calculations show that in naphthalene (1) and its cyclopenta-fused congeners acenaphthylene (2), pyracylene (3), and cyclopenta[*b,c*]acenaphthylene (4), as well as in fluoranthene (5) and cyclopenta[*c,d*]fluoranthene (6), the  $6\pi$ -electron conjugated circuits (benzene-like) have the highest contribution to the resonance energy ( $E_{\text{res}}$ ). Other conjugated circuits do not contribute. The total resonance energy ( $E_{\text{res}}$ ) of the compounds is thus not affected by cyclopenta-fusion. Thus at least in the ground state the five-membered rings should be seen as alkene substituents; they do not participate in the delocalized  $\pi$ -system. This is corroborated by the calculation on 4-H<sub>2</sub>, which gave essentially the same results as the calculation on 4. The additional five-membered ring influences the naphthalene core as a substituent by increasing the strain on the naphthalene subunit (cf. also refs 15 and 16).

The changes in the ab initio VB resonance energies ( $E_{\text{res}}$ ) agree with those in aromatic stabilization energies (ASEs), evaluated using isodesmotic reactions. The trends in the  $\pi$ -electron conjugated-circuits-model resonance energies ( $E_{\text{res}}^{\text{cc}}$ ) do not coincide with the ab initio VB resonance energies ( $E_{\text{res}}$ ). Notwithstanding, the relative energy differences between individual structures can be estimated using this model.

Thus it appears to be a general rule that peripheral cyclopenta-fusion of PAHs will exert only a moderate effect on the resonance energy ( $E_{\text{res}}$ ) of the parent PAH. Furthermore, the changes in magnetic properties do not correlate directly with the changes in resonance energies  $E_{\text{res}}$ .

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**Supporting Information Available:** Cartesian coordinates of the RHF/6-31G optimized geometries of 1–6. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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