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Aromaticity Evaluations of Planar [6]Radialenes

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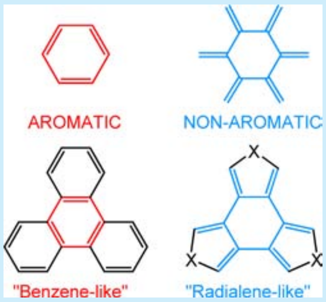
Supporting Information

ABSTRACT: The aromatic character of fused polycyclic systems varies with the nature of their annulated rings. Computed extra cyclic resonance energies (ECREs) reveal that the central six membered rings (6MRs) of the heterocyclic fused congeners **1−5** are "[6]radialene-like", but that the central 6MRs of triphenylene **9**, coronene **10**, and isocoronene **11** are "benzene-like." Comparisons with geometric (harmonic oscillator model of aromaticity, HOMA) and magnetic (nucleus independent chemical shifts, NICS) criteria illustrate the multifaceted nature of aromaticity in **1−11**.



The possible aromaticity of [6]radialene **1a** and of its derivatives **1−5** (Figure 1) is intriguing because, like benzene, their central six-membered rings (6MRs) are comprised exclusively of sp^2-hybridized carbons.[1] Although the parent [6]radialene **1a** is highly nonplanar, hetero-[6]radialenes **1b−c** and the well-characterized 5MR annulated systems **2−5**, are planar.[2,3] The latter have often been used as π-electron acceptors in materials chemistry,[4] but their aromaticity has not been systematically analyzed.[5]

We now report a detailed study of the influence of the annulated rings and of the exocyclic C═C, C═O, and C═N bonds on the aromatic character of the central ring of planar [6]radialenes **1−5** and of heteroaromatics **6−8**. The results are compared with the aromaticity of the central 6MRs of triphenylene **9**, coronene **10**, and isocoronene **11** (Figure 1).[6] Our analysis of the aromatic character of **1−11** is based on geometric (harmonic oscillator model of aromaticity HOMA),[7] magnetic (nucleus-independent chemical shift, NICS),[8] and energetic (extra cyclic resonance energy ECRE)[9] criteria. All geometries were optimized at the B3LYP/6-31G(d) level employing Gaussian 03.[10] For comparison, optimized geometries and calculated HOMA values for selected compounds were performed at the B3PW91/aug-cc-pVDZ level and included in the Supporting Information (SI). The HOMA index can be dissected into two independent contributions (eq 1) describing the effect of π-electron delocalization: EN, the mean bond length of a ring system, and GEO, the degree of ring bond length alternation.[7]

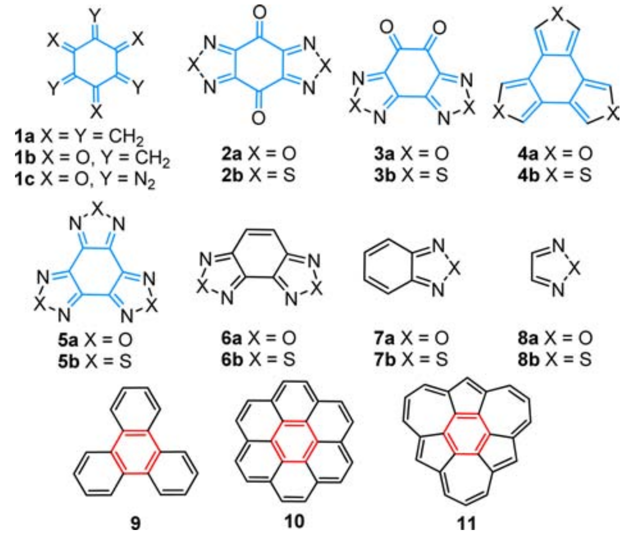


Figure 1. [6]Radialenes **1a−c**, polycyclic systems with planar [6]radialene cores **2−5**, heteroaromatics **6−8**, triphenylene **9**, coronene **10**, and isocoronene **11**.

$$\text{HOMA} = 1 - \text{EN} - \text{GEO} \tag{1}$$

The HOMA, EN, and GEO parameters of benzene and **1−11** are listed in Table 1. Positive HOMA values indicate aromaticity; negative HOMAs indicate antiaromaticity or reduced aromatic character.

Notably, the benzene HOMA (+0.98) and the values for **1a−c** have opposite signs. Although both benzene and [6]radialenes **1a−c** have equalized ring CC bond lengths (GEO = 0), the mean ring CC lengths of **1a−c** (up to 1.503 Å, large EN) are much longer than those of benzene (1.395 Å, EN ≈ 0).[11] The central rings of coronene **10** (+0.60) and isocoronene **11** (+0.84) are only somewhat less aromatic than that of benzene (+0.98), while the central ring of triphenylene **9** has significantly reduced aromatic character (+0.05).

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Table 1. Computed HOMA, EN, and GEO for Benzene, Planar [6]Radialenes 1a−c, and the Central 6MRs of the Polycyclic Systems 2−7 and 9−11

compound[a]	HOMA	EN	GEO
benzene[b]	0.98	0.021	0.000
1a (D_{6h})	−2.40[c]	3.399	0.000
1b[d]	−2.15	3.148	0.000
1c[d]	−0.81	1.805	0.000
2a	−1.15	1.927	0.223
2b	−1.36	2.163	0.198
3a	−1.74	2.103	0.637
3b	−1.82	2.336	0.485
4a	−0.08	1.077	0.000
4b	−0.18	1.165	0.011
5a	0.18	0.807	0.010
5b	−0.10	1.097	0.007
6a	0.32	0.415	0.264
6b	0.19	0.519	0.290
7a	0.62	0.138	0.244
7b	0.59	0.160	0.251
9	0.05	0.818	0.134
10	0.60	0.400	0.000
11	0.84	0.022	0.139

[a] HOMA(5MR) = +0.68 for **8a**; see ref 7. [b] See ref 6a. [c] −2.41 for nonplanar D_{3d} [6]radialene; ref 7c. [d] Reference 2.

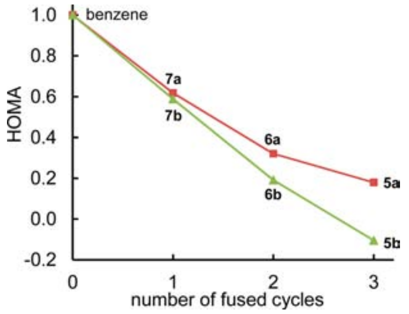


Figure 2. Changes in HOMA upon the annulation of benzene with one **7a−b**, two **6a−b**, and three **5a−b** [1,2,5]-oxadiazole (red squares) or [1,2,5]-thiadiazole (green triangles) rings.

As shown in Figure 2, the 6MRs of **7a−b**, **6a−b**, and **5a−b** display increasing "[6]radialene-character" and less positive HOMA values when fused to one, two, and three heterocyclic 5MRs. Like benzene, the 6MRs of **5a−b** (and the isoelectronic **4a−b**) have nearly equal ring CC bond lengths (GEO ≈ 0), but benzannulation elongates their mean lengths (up to 1.462 Å).[11] However, increased ring bond alternation results when one of the 5MRs of **5a−b** is replaced by two C=O bonds to give **3a−b**. The CC bonds in the quinones, **2a−b** and **3a−b**, exhibit substantial elongation (up to 1.573 Å), and their 6MRs have large negative HOMA values, close to those of **1a−c**.[11] For comparison, the HOMA value for 1,4-benzoquinone (−0.83, two exocyclic C=O bonds) also is negative, indicative of substantially reduced aromatic character, or even of antiaromaticity.[12]

Table 2. Computed Dissected 6MR-NICS(0)$_{\pi zz}$ (in ppm, at PW91/IGLOIII), BLW-REs (Adiabatic, at B3LYP/6-31G(d)), and 6MR-ECREs, for Benzene, for the 6MRs of 1−7 and 9−11 and for the 5MRs of 8a−b (See Text)

compound	NICS(0)$_{\pi zz}$	BLW-RE	6MR-ECRE
benzene	−36.9	61.39	+29.98
1a (D_{6h})	−1.2	54.28	−8.54
1b	+0.6	57.86	−3.94
2a	+4.4	129.27	+9.63
2b	+5.8	128.16	+12.22
3a	+4.6	131.99	+6.91
3b	+7.6	125.28	+9.34
4a	−22.8	195.70	−0.08
4b	−21.0	166.67	+2.90
5a	+3.6	175.61	+9.35
5b	+3.6	168.55	+11.92
6a	−7.2	128.62	+2.88
6b	−13.4	123.96	+4.64
7a	−24.9	87.93	+7.14
7b	−29.1	86.81	+9.23
8a	−28.7	47.82	+15.38
8b	−30.7	44.61	+18.33
9	−13.5	218.88	+34.71
10	−2.4	317.38	+28.54
11	−42.4	247.35	+43.23

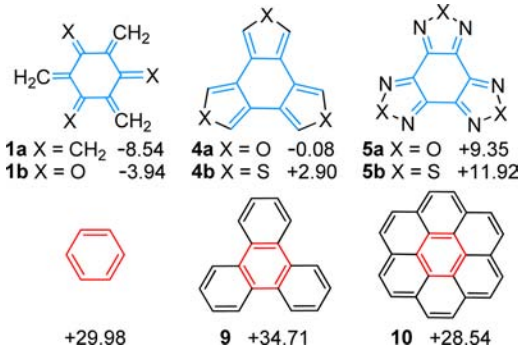


Figure 3. Computed 6MR-ECREs (in kcal/mol) for the central 6MRs of planar [6]radialenes **1**, **4**, **5** and for benzene, **9**, and **10**. The 6MRs being considered are highlighted in blue for "[6]radialene-like" and in red for "benzene-like" rings.

The extra cyclic resonance energies (ECREs) were computed employing the block-localized wave function (BLW) method[13] to quantify the aromatic stabilization energies associated with the "[6]radialene units" of **1−5** and the central 6MR of **9−11** (Table 2 and Figure 3). BLW-REs (REs, resonance energies) were evaluated by the computed energy difference between the fully delocalized wave function (Ψ_{deloc}) of the molecule of interest and that of its hypothetical "localized" wave function (Ψ_{loc}), in which π-conjugations between each of the double bonds are mathematically "disabled" (BLW-RE = $\Psi_{loc} - \Psi_{deloc}$).[13]

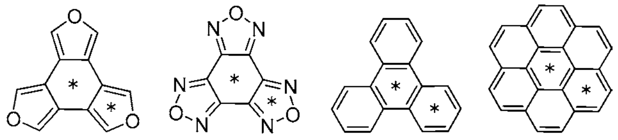
All 6MR-ECRE data were derived by the computed BLW-RE difference between that of the compound being considered minus that of the fused 5- or 6-MR(s) and π-conjugated units in the system (Table 2). For example, in coronene **10**, the 6MR-ECRE for the central ring (+28.54 kcal/mol) is derived by the computed BLW-RE for **10** (317.38 kcal/mol) minus the BLW-REs of three benzene rings (61.39 × 3), six *anti*-butadienes (12.21 × 6), and three *syn*-butadienes (10.47 × 3). Based on this procedure, the computed 6MR-ECREs for **1−11** evaluate only the aromatic stabilization energy of the ring considered (Figure 3, central 6MR rings).

Six membered rings with large positive 6MR-ECRE values are aromatic and "benzene-like" whereas those with negative or close to zero 6MR-ECRE values are "[6]radialene-like." For reference, the computed ECRE for benzene is +29.98 kcal/mol, but that of planar [6]radialene, **1a** (D_{6h}), is −8.54 kcal/mol (note opposite sign). The ECRE of benzene is evaluated by its BLW-RE minus that of three *syn*-butadienes. The ECRE for **1a** is evaluated by the difference between its BLW-RE and that of six *syn*-butadienes. Direct comparisons of the computed 6MR-ECREs of **2−11** to those of benzene and of **1a** reveal the nature of the 6MR considered (Figure 3).

Remarkably, the type of ring annulation largely dictates the nature of the central 6MRs in **2−11**. According to their 6MR-ECREs, the *benzo-fused* central rings of **9** (+34.71 kcal/mol) and **10** (+28.54 kcal/mol) are "benzene-like" (Figure 3, in red), but the *heterocyclic 5MR-fused* six-membered rings of **4−5** (6MR-ECREs ranging from −0.08 to +11.92) are weakly stabilized aromatically and display "[6]radialene-like" character (Figure 3, in blue). For comparison, the central 6-MR of isocoronene **11** is the most aromatically stabilized (+43.23 kcal/mol).[6c−e] Thus, despite also having three annulated rings, the 6MR-ECRE of **9** is three times larger compared to that of **5a−b** (Figure 3). Changes in the *number* of fused rings may have less energetic impact. Thus, the 6MR-ECREs of **7a** (+7.14 kcal/mol, one fused ring), **6a** (+2.88 kcal/mol, two fused ring), and **5a** (+9.35 kcal/mol, three fused ring) differ much less; all are within +10 kcal/mol (Table 2).

Comparisons of the energetic (6MR-ECRE) and the magnetic (dissected NICS$_{\pi zz}$) criteria for the central ring of **9−11** and for the [6]radialene units of **1−7** elucidate the multifaceted nature of aromaticity in polycyclic systems. Dissected LMO[8c] (localized molecular orbital)-NICS(0)$_{\pi zz}$ values (at the PW91/IGLOIII level) were computed at the central ring of **1−11** to quantify their magnetic aromatic character (see Table 2). LMO-NICS distinguishes magnetic shielding contributions from each of the σ-bonds, π-bonds, and lone pairs. NICS$_{\pi zz}$ is the most refined NICS index for quantifying π-aromaticity, as it extracts the out-of-plane tensor component of the isotropic NICS and includes contributions only from the π MOs.[8c] For monocyclic systems, aromatic rings have negative NICS(0)$_{\pi zz}$ values (diatropic) and antiaromatic rings have positive NICS(0)$_{\pi zz}$ values (paratropic). However, in polycyclic systems, the interplay among multiple ring currents can lead to "artifactually" reduced diatropicity (e.g., in both the inner and outer 6MRs of **10**, as discussed below) or enhanced paratropicity [e.g., in the central 6MRs of **2−5**] for the individual rings examined.[14]

In apparent agreement with Aihara, et al.,[6f] the computed NICS(0)$_{\pi zz}$ for both **9** and **10** suggest lower aromatic character for the central rings; but this is misleading (see below). The NICS behavior of the central rings in both **9** and **10** are influenced by the deshielding of the outer rings. Thus, **1a** (−1.2 ppm), **1b** (+0.6 ppm), and the central ring of coronene **10** (−2.4 ppm) all have NICS(0)$_{\pi zz}$ values close to zero (Table 1), but their 6MR-ECREs differ drastically (−8.54, −3.94, and +28.54 kcal/mol, respectively). The monocyclic planar [6]radialenes **1a−b** are nevertheless nonaromatic, but the central ring of **10** is almost as aromatic as benzene (see ECREs in Figure 3). In **10**, the *magnetic* aromaticity of the central ring is lowered "artifactually," as it resides in the joint *deshielded* region of six (outer) aromatic rings. In contrast, the diatropicities of each of the outer 6MRs of **10** (NICS(0)$_{\pi zz}$ = −17.0 ppm, Figure 4) maintain half of the aromatic character of benzene, as they reside in the *deshielding* regions of only three neighboring aromatic rings. In **9**, the corresponding inner (−13.5 ppm, three adjacent aromatic rings) and outer (−36.1 ppm, one adjacent aromatic ring, bottom right) six-membered rings have more negative NICS(0)$_{\pi zz}$ values (Figure 4), since they are deshielded by fewer adjacent aromatic rings. In isocoronene **11**, the central 6-MR (NICS(0)$_{\pi zz}$ = −42.4 ppm) as well as outer 5-MRs (NICS(0)$_{\pi zz}$ = −38.6 ppm) and 7-MRs (NICS(0)$_{\pi zz}$ = −53.5 ppm) are all highly aromatic, due to a peripheral ring current.[6]


4a −22.8 (inner) −25.3 (outer)

5a +3.6 (inner) −29.3 (outer)

9 −13.5 (inner) −36.1 (outer)

10 −2.4 (inner) −17.0 (outer)

Figure 4. Computed NICS(0)$_{\pi zz}$ values (in ppm, at PW91/IGLOIII) at the individual ring centers (NICS point indicated by black star) of **4a**, **5a**, and **9−10**.

The more negative NICS(0)$_{\pi zz}$ values of the 6MRs of **4a** (−22.8 ppm) vs **5a** (+3.6 ppm) also are the result of the more deshielded central 6MR in **5a** (Figure 4). Since N's are more electronegative than C's, the N-containing 5MRs (NICS(0)$_{\pi zz}$ = −29.3 ppm) of **5a** competes more effectively for π-aromaticity and deshields the central 6MR (+3.6 ppm). In **4a**, both the outer (5MR, −22.8 ppm) and inner (6MR, −25.3 ppm) rings are nearly equally aromatic. Thus, the 6MR of **5a** is magnetically more "[6]radialene-like" while that of **4a** is more "benzene-like."

Likewise, the sequential annulation of benzene (NICS(0)$_{\pi zz}$ = −36.9 ppm) with one **7a−b** (6MR-NICS(0)$_{\pi zz}$ = −24.9, −29.1 ppm), two **6a−b** (−7.2, −13.4 ppm), and three **5a−b** (+3.6, +3.6 ppm) 5MRs result in increasingly less negative NICS(0)$_{\pi zz}$ values, since the 6MRs become increasingly *deshielded* (see Table 1). For the same reason, the central rings of **2a−b** and **3a−b** have positive 6MR-NICS(0)$_{\pi zz}$ values (+4.4 to +7.6 ppm, Table 2) but are not antiaromatic (cf. positive 6MR-ECRE values ranging from +6.9 to +12.2 kcal/mol, Table 2).

Depending on the nature of their annulated rings, fused benzenoids can have either "benzene-like" (aromatic) or "[6]radialene-like" (nonaromatic) character. As the aromatic character of polycyclic systems is multifaceted, aromaticity evaluations based on geometric, magnetic, and energetic criteria do not always agree, but provide complementary insights.[15]

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Cartesian coordinates and energies for all optimized species. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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(10) Gaussian 03 (complete citation included in the SI).

(11) For the X-ray structure of **1c**, see ref 2c; for **4b**, see ref 5b; for **5a−b**, see ref 3a and 3e. For computed bonds lengths and energies for **1−11**, see the SI.

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