

Aromaticity and diatropicity of *p*-polyphenyl- α,ω -quinododimethides

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Abstract *p*-Polyphenyl- α,ω -quinododimethides were predicted to be moderately aromatic and diatropic, although they exist only in a single classical resonance structure with no aromatic conjugated circuits. Such a dichotomy was resolved using our graph theory of aromaticity and ring-current diamagnetism. Six-site non-conjugated circuits were found to contribute appreciably to aromaticity and ring-current diamagnetism. Within each quinododimethide molecule, local aromaticity increases on going from the outermost to inner phenylene rings.

Keywords *p*-Polyphenylquinododimethides · *p*-Polyphenyl · Aromaticity · Ring-current diamagnetism · Graph theory

1 Introduction

The conjugated circuit model of aromaticity states that conjugated circuits are the main origin of aromaticity in polycyclic aromatic hydrocarbons [1,2]. Dewar resonance energies of polycyclic benzenoid hydrocarbons [3] can be reproduced well in terms of conjugated circuits [1,2]. Non-conjugated circuits have been regarded as minor contributors to global aromaticity. In 1975, we tacitly assumed that polyacene-2,3-quinododimethides are olefinic or polyene-like in nature, because only one classical resonance structure can be written for them [4]. Conjugated circuits are missing in these hydrocarbons. Schleyer and Puhlhofer also used such a hydrocarbon with exocyclic

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methylenes as a polyene-like reference structure to estimate the aromatic stabilization energy of a like cyclic π -system [5].

In 1973, nevertheless, Gleicher et al. found that a series of polyacene-2,3-quinododimethides might be moderately aromatic with positive Hess-Schaad and Dewar resonance energies [6]. There seemed to be a steady increase in resonance energy per π -electron on going from *p*-xylylenes to higher homologues. Thus, even polycyclic semibenzenoid hydrocarbons that consist of essential single and double bonds might possibly be aromatic if they are sufficiently large in molecular size. Recently, fulminene-2,10-quinodimethide, which also exists only in a single classical resonance structure, was predicted to have proton chemical shift values on the aromatic range [7,8].

We then examined such anomalous aromatic and diatropic character of polyacene-2,3-quinododimethides [9] using our graph theory of aromaticity and ring-current diamagnetism [10–25] and found that, for these hydrocarbons, many non-conjugated circuits contribute much to aromaticity and diatropicity. As an extension of this work, we attempt to explore aromatic and diatropic character of *p*-polyphenyl- α,ω -quinododimethides using the same theory. At first glance, these hydrocarbons appear to be much more polyene-like than polyacene-2,3-quinododimethides. Only one resonance structure can be written for these hydrocarbons.

2 Theory

Our graph theory of aromaticity and ring-current diamagnetism was constructed within a simple Hückel framework. We use a topological resonance energy (TRE) as an indicator of global aromaticity [10–12]. Percentage TRE (% TRE) is defined as 100 times TRE, divided by the total π -binding energy of the polyene reference [12, 17, 19]. This quantity is useful as a measure of aromaticity, normalized with respect to the molecular size. Bond resonance energy (BRE) represents the contribution of a given π -bond to the global aromaticity [17–20]. We pointed out that the BRE from a peripheral π -bond can be used as an indicator of local aromaticity for the ring to which the π -bond belongs [20]. For simplicity, all molecules are assumed to be planar with all rings being regular hexagons.

Circuit resonance energy (CRE) has been interpreted as an energy gain or loss due to cyclic conjugation along a given circuit [21–25]. Circuits stand for all possible cyclic or closed paths that can be chosen from a cyclic π -system [26]. The CRE for the *i*th circuit in a polycyclic π -system *G* is defined as A_i in the form [12, 21–25]:

$$A_i = 4 \sum_j^{\text{occ}} \frac{P_{G-r_i}(X_j)}{P_G(X_j)} \quad (1)$$

where r_i is a set of carbon atoms that constitute the *i*th circuit c_i ; $G-r_i$ is the subsystem of *G*, obtained by deleting from *G* all carbon atoms that constitute the *i*th circuit; $P_G(X)$ and $P_{G-r_i}(X)$ are the Hückel characteristic polynomials for *G* and $G-r_i$, respectively; and X_j is the *j*th largest root of the equation $P_G(X) = 0$; and *j* runs over all occupied

π molecular orbitals. If some occupied molecular orbitals have the same energies, this formula must be replaced by others [13–15].

The sum of A_i values or CREs over all circuits represents the aromatic stabilization energy for an entire π -system. This sum is termed a magnetic resonance energy (MRE), which means a TRE-like quantity derived from the magnetic response of a cyclic π -system [21–25]:

$$\text{MRE}/|\beta| = \sum_i^G A_i \quad (2)$$

where β is the standard resonance integral between two adjacent carbon $2p_z$ orbitals. An excellent correlation was observed between MRE and TRE for polycyclic benzenoid hydrocarbons and heterocycles [21, 23, 25]. Note that no hypothetical polyene reference is needed to evaluate the MRE.

In fact, A_i appears in our formula for ring-current magnetic susceptibility [12]:

$$\chi_G = 4.5\chi_0 \sum_i^G A_i \left(\frac{S_i}{S_0} \right)^2 \quad (3)$$

where χ_0 is the ring-current susceptibility of benzene; S_i and S_0 are the areas of r_i and the benzene ring, respectively. Positive and negative A_i values represent diamagnetic and paramagnetic contributions, respectively. From this formula we can derive the contribution of the i th circuit to χ_G in the form [12–14]:

$$\chi_i = 4.5\chi_0 A_i \left(\frac{S_i}{S_0} \right)^2 \quad (4)$$

Every circuit is supposed to sustain a π -electron current in the external magnetic field, the intensity of which is given by [14–16]:

$$I_i = 4.5I_0 A_i \frac{S_i}{S_0} \quad (5)$$

where I_0 is the intensity of a π -electron current induced in the benzene ring. Positive and negative A_i values now represent diatropicity and paratropicity, respectively. Thus, at the level of individual circuits, aromaticity and antiaromaticity exactly correspond to diamagnetism and paramagnetism, respectively. In general, a total π current density map for a polycyclic π -system can be obtained by superposing all the circuit currents.

3 Results and discussion

p-Polyphenyls (1–8) and *p*-polyphenyl- α,ω -quinododimethides (9–16) studied are shown in Fig. 1. These two sets of polycyclic hydrocarbons are not condensed ones; all circuits are six-site ones with essentially the same areas, being separated spatially

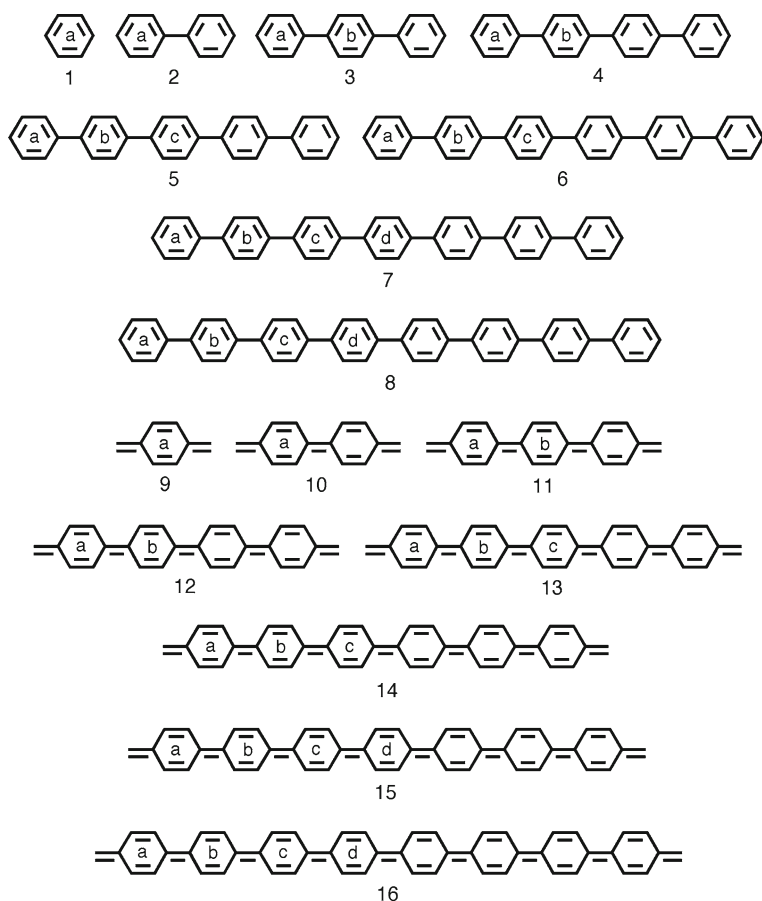


Fig. 1 *p*-Polyphenyls (1–8) and *p*-polyphenyl- α,ω -quinododimethides (9–16) studied

from each other. The number of circuits is necessarily equal to that of six-membered rings. BREs for CC bonds that do not belong to any ring vanish. These π -bonds do not sustain ring currents.

TREs, MREs, and ring-current diamagnetic susceptibilities (χ_G) for 1–16 are listed in Table 1. Non-zero BREs are presented in Table 2. The intensities of diamagnetic ring currents induced in 1–16 are summarized in Table 3. For all circuits in 1–16, S_i is assumed to be S_0 , so that the portion of ring-current susceptibility attributable to a given ring (i.e., χ_i) is proportional not only to the intensity of the ring current but also to the CRE. Therefore, CRE can be calculated without using Eq. 1. That is, CRE in units of $|\beta|$ is equal to the current intensity in units of I_0 divided by 4.5. CREs thus obtained for all circuits (i.e., all rings) in 1–16 are presented in Table 4. It follows that the ring-current susceptibility in units of χ_0 , divided by 4.5, is equal to the MRE in units of $|\beta|$. As far as 1–16 are concerned, χ_G can be used as a measure of global aromaticity [27,28].

Table 1 Topological resonance energies (TREs), magnetic resonance energies (MREs), and ring-current diamagnetic susceptibilities (χ_G) for *p*-polyphenyls and *p*-polyphenyl- α , ω -quinododimethides

Species	TRE ^a ($ \beta $)	MRE ($ \beta $)	χ_G (χ_0)
<i>p</i> -Polyphenyls			
1	0.2726 (3.528)	0.2222	1.0000
2	0.5017 (3.159)	0.4155	1.8696
3	0.7267 (3.022)	0.6067	2.7300
4	0.9505 (2.954)	0.7975	3.5885
5	1.1740 (2.908)	0.9882	4.4468
6	1.3974 (2.879)	1.1789	5.3049
7	1.6207 (2.858)	1.3696	6.1630
8	1.8440 (2.842)	1.5602	7.0211
<i>p</i> -Polyphenyl- α , ω -quinododimethides			
9	0.0612 (0.621)	0.0593	0.2667
10	0.1948 (1.086)	0.1886	0.8489
11	0.3771 (1.449)	0.3624	1.6308
12	0.5865 (1.717)	0.5562	2.5030
13	0.8097 (1.914)	0.7560	3.4022
14	1.0387 (2.059)	0.9555	4.2999
15	1.2695 (2.167)	1.1528	5.1875
16	1.5000 (2.247)	1.3478	6.0653

^a Values in parentheses are % TREs

Table 2 Bond resonance energies (BREs) for *p*-polyphenyls and *p*-polyphenyl- α , ω -quinododimethides

Species	BRE ($ \beta $)			
	Ring a	Ring b	Ring c	Ring d
<i>p</i> -Polyphenyls				
1	0.2726			
2	0.2538			
3	0.2521	0.2356		
4	0.2518	0.2339		
5	0.2518	0.2336	0.2321	
6	0.2518	0.2336	0.2318	
7	0.2518	0.2336	0.2318	0.2115
8	0.2518	0.2336	0.2318	0.2315
<i>p</i> -Polyphenyl- α , ω -quinododimethides				
9	0.0612			
10	0.1003			
11	0.1156	0.1668		
12	0.1234	0.1900		
13	0.1275	0.2004	0.2120	
14	0.1297	0.2055	0.2202	
15	0.1309	0.2080	0.2237	0.2264
16	0.1314	0.2093	0.2253	0.2286

Figure 2 shows a plot of MRE against TRE for **1–16**. An excellent correlation is found between these two quantities with a correlation coefficient of 0.997. This indicates that not only TRE but also MRE can be used as a reliable indicator of global aromaticity. In fact, these two sets of hydrocarbons exhibit slightly different colinearities. An approximate value for BRE can be obtained by dividing the CRE by

Table 3 Intensities of ring currents for *p*-polyphenyls and *p*-polyphenyl- α,ω -quinododimethides

Species	Intensity of a ring current (I_0)			
	Ring a	Ring b	Ring c	Ring d
<i>p</i> -Polyphenyls				
1	1.0000			
2	0.9348			
3	0.9294	0.8712		
4	0.9287	0.8656		
5	0.9286	0.8649	0.8599	
6	0.9285	0.8647	0.8592	
7	0.9285	0.8647	0.8590	0.8584
8	0.9285	0.8647	0.8590	0.8583
<i>p</i> -Polyphenyl- α,ω -quinododimethides				
9	0.2667			
10	0.4244			
11	0.4829	0.6650		
12	0.5119	0.7396		
13	0.5272	0.7714	0.8049	
14	0.5352	0.7867	0.8280	
15	0.5394	0.7943	0.8378	0.8447
16	0.5415	0.7980	0.8423	0.8508

Table 4 Circuit resonance energies (CREs) for *p*-polyphenyls and *p*-polyphenyl- α,ω -quinododimethides

Species	CRE ($ \beta $)			
	Ring a	Ring b	Ring c	Ring d
<i>p</i> -Polyphenyls				
1	0.2222			
2	0.2077			
3	0.2065	0.1936		
4	0.2064	0.1924		
5	0.2063	0.1922	0.1911	
6	0.2063	0.1922	0.1909	
7	0.2063	0.1922	0.1909	0.1908
8	0.2063	0.1922	0.1909	0.1907
<i>p</i> -Polyphenyl- α,ω -quinododimethides				
9	0.0593			
10	0.0943			
11	0.1073	0.1478		
12	0.1138	0.1644		
13	0.1172	0.1714	0.1789	
14	0.1189	0.1748	0.1840	
15	0.1199	0.1765	0.1862	0.1877
16	0.1203	0.1773	0.1872	0.1891

4.5. Both of these two quantities can be used as indicators of local aromaticity [20]. Thus, our graph theory allows us to interpret the TRE, BRE, π current density, and χ_G consistently in terms of CREs.

We first survey the aromaticity and ring-current diamagnetism of *p*-polyphenyls (1–8). One can write 2^N classical resonance structures for 1–8, where N is the number of benzene rings. These benzenoid hydrocarbons are highly aromatic with large

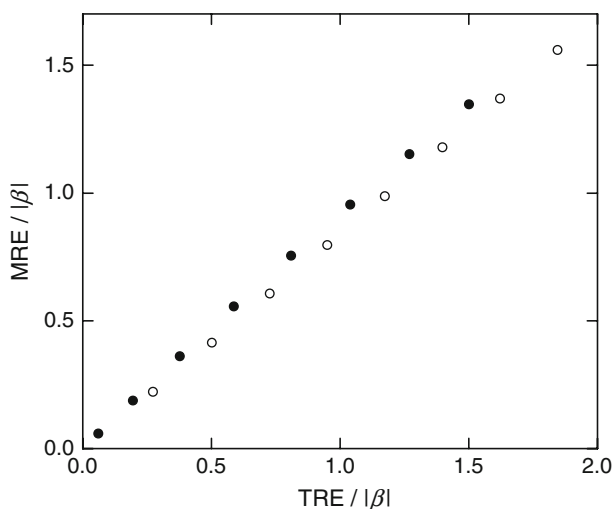


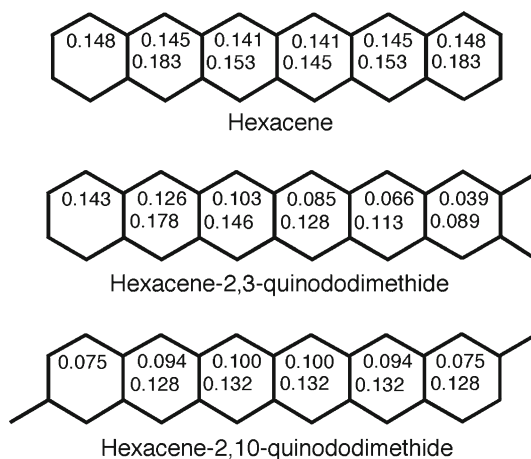
Fig. 2 Correlation between TREs and MREs for *p*-polyphenyls (○) and *p*-polyphenyl- α,ω -quinododimethides (●)

positive % TREs. All constituent benzene rings exhibit large positive BREs and sustain large diamagnetic currents when the molecules are placed in the magnetic field. All benzene rings are rather similar in local aromaticity to each other. Average local aromaticity decreases to some extent on going from benzene to higher *p*-polyphenyls, since inner rings are slightly less aromatic than edge rings. High aromaticity of **1–8** conform to the fact that they are a kind of fully benzenoid hydrocarbons in Clar's terminology [29,30]. All benzene rings are sextet rings [29,30] and carry aromatic six-site conjugated circuits with them.

We then examine the aromaticity and ring-current diamagnetism of *p*-polyphenyl- α,ω -quinododimethides (**9–16**). These hydrocarbons have been expected to be non-aromatic in nature, because neither sextet rings nor conjugated circuits can be chosen from the π -system. All the CC single and double bonds in the classical resonance structures are fixed ones. However, these hydrocarbons were found to be still aromatic with positive TREs and MREs and sustain diamagnetic ring currents. It is true that each quinododimethide is less aromatic with a smaller % TRE than the corresponding *p*-polyphenyl. Exomethylenes suppress not only cyclic conjugation but also circulation of π -electrons to some extent.

As can be seen from the BREs in Table 2 and CREs in Table 4, the density of local aromaticity in **9–16** is higher in inner rings. It seems likely that the perturbation produced on the inner rings by the exomethylenes rapidly decrease as the number of hexagonal rings increases. As a result, a diamagnetic current is fairly strong in the inner rings. The % TRE then increases on the elongation of the *p*-polyphenyl moiety. *p*-xylylene (**9**) retains only 20% of the TRE for benzene (**1**). In marked contrast, *p*-octaphenyl- α,ω -quinododimethide (**16**) retains more than 80% of the % TRE for *p*-octaphenyl (**8**). Thus, higher members of the *p*-polyphenyl- α,ω -quinododimethide series are far from being non-aromatic cyclic polyenes. They indeed are

Fig. 3 BREs in units of $|\beta|$ for hexacene, hexacene-1,2-quinododimethide, and hexacene-1,10-quinododimethide



aromatic species. TRE for **8** is 6.8 times as large as that for **1**, whereas TRE for **16** is 24.5 times as large as that for **9**.

In this context, large polyacene-2,3-quinododimethides were predicted to be moderately aromatic and sustain moderately strong ring currents, although only one classical resonance structure can be written for them [9]. Such hydrocarbons are exemplified by two hexacenequinododimethides in Fig. 3. As seen from this figure, the hexagonal rings of large local aromaticity are again those located further from the exomethylenes. Non-conjugated circuits must likewise contribute appreciably to the aromaticity and ring-current diamagnetism of these hydrocarbons. Now, not only polyacene-1,2-quinododimethides but also *p*-polyphenyl- α,ω -quinododimethides proved to be aromatic, although no conjugated circuits can be chosen from the π -system. This aspect of quinododimethides can partly be justified by the extended Hückel rule proposed by Hosoya et al. [31,32]. This rule states that all six-site circuits are aromatic in nature whether they are conjugated ones or not.

4 Concluding remarks

p-Polyphenyl- α,ω -quinododimethides were predicted to be more or less aromatic and diatropic, although they have no conjugated circuits. Such an apparent dichotomy with respect to aromatic character was interpreted using our graph theory of aromaticity and ring-current diamagnetism. Non-conjugated six-site circuits contribute appreciably to aromaticity and ring-current diamagnetism in these hydrocarbons. At least, six-membered rings far from the exomethylenes exhibit considerable local aromaticity. One, however, should remember that *p*-polyphenyl- α,ω -quinododimethides must still be kinetically very unstable even though they are moderately aromatic. They are supposed to be chemically reactive, because all or some of the rings would tend to convert into fully aromatic benzene rings.

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