Aromaticity and Superaromaticity in Cyclopolyacenes

Jun-ichi Aihara
Department of Chemistry, Faculty of Science, Shizuoka University, Oya, Shizuoka 422, Japan

The topological resonance energy (TRE) method has been applied to linear and zigzag isomers of cyclopolyacenes to investigate their aromatic character. In general, zigzag cyclopolyacenes are found to be highly aromatic. Every linear cyclopolyacene is much less aromatic than the zigzag isomer, and large linear and zigzag cyclopolyacenes are as aromatic as their respective polyacenes. A Hückel-like rule is observed for linear cyclopolyacenes. A super-ring structure scarcely affects the aromatic character of sizeable cyclopolyacenes.

A super-ring molecule is formed by rolling a polyacene molecule into a ring with one edge benzene ring folding onto the other one. Such a hydrocarbon may be called a cyclopolyacene or cyclacene.[1–3] As shown in Fig. 1, there are two types of cyclopolyacenes: linear and zigzag. The synthesis of cyclopolyacenes has long been a challenging target in organic chemistry; however, to date nobody has succeeded in preparing any of them. Stoddart and co-workers synthesized octahydro derivatives of linear cyclododecacene and cyclotetradecacene.[1–3] A space-filling molecular model of linear cyclooctadecacene was used as a symbol of the seventh international symposium on the chemistry of novel aromatic compounds (ISNA-7) held at Victoria, British Columbia, Canada in 1992.

Cyclopolyacenes also have attracted theoreticians' attention.[4–10] In 1980 Gutman derived an analytical formula for the energies of the π-electron molecular orbitals for linear cyclopolyacenes.[5] In 1983 Tanaka and co-workers[6] and Kivelson and Chapman[7] discussed the possibility of infinite linear polyacenes or cyclopolyacenes as synthetic metals. Hosoya and co-workers elaborately derived analytical formulae for the characteristic polynomials of linear and zigzag cyclopolyacenes.[8,9] Most of the theoretical studies were based on simple Hückel theory or the equivalent in solid-state physics.

Inherent properties of a cyclic π-electron molecule have been referred to as aromaticity. As early as 1975 we discussed the possible non-aromatic nature of very large linear cyclopolyacenes.[4] We feel it an urgent matter to investigate the aromatic character of cyclopolyacenes in order to assess their synthetic possibility. The topological resonance energy (TRE) is known to be a good measure of aromatic stabilization.[11–13] In this paper we analyse the TREs of linear and zigzag cyclopolyacenes. Predicted aromaticities in cyclopolyacenes are compared with those in polyacenes.

Theory

Simple Hückel theory was utilized to evaluate the TREs of polyacenes and cyclopolyacenes.[11–13] The percentage resonance energy (%RE) and the resonance energy per π electron (REPE) are useful to allow comparison of aromaticities in different molecules.[12–17] The %RE is given as 100 times the TRE, divided by the total π-binding energy of the graph-theoretically defined polyene reference.[15–17] The REPE is the TRE divided by the number of π electrons.[12–14]

In the TRE method, we assume that both a real molecule and the polyene reference are equally strained. The same β value is assigned to all resonance integrals in the two structures. No correction for the curvature of a molecule is made. The %RE is independent of the curvature of a molecule because it is a dimensionless quantity. For this reason, we will discuss aromatic character of curved molecules using the %RE values. It should be noted that the TRE method has been applied successfully to fullerene conjugated systems.[15–17]

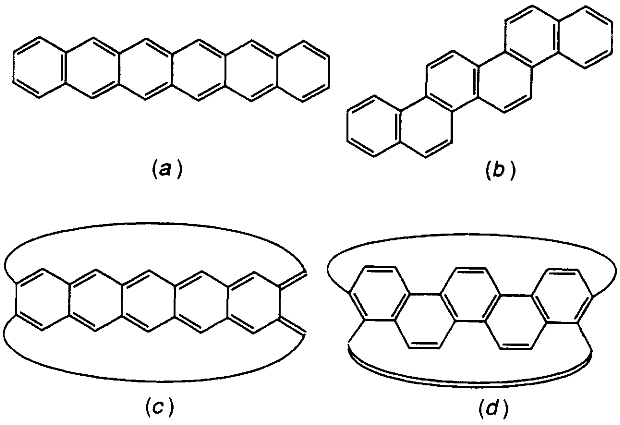

Fig. 1 Kekulé structures of (*a*) linear hexacene; (*b*) zigzag hexacene; (*c*) linear cyclohexacene and (*d*) zigzag cyclohexacene

The localization energy is a typical index for determining the tendency to undergo addition or substitution reactions.[18,19] The smallest localization energy (SLE) in a molecule points to its most reactive site. Thus, chemical reactivity of a molecule is primarily determined by the magnitude of the SLE. The highest occupied molecular orbital–lowest unoccupied molecular orbital (HOMO–LUMO) energy separation has also been used as a rough measure of chemical reactivity.[20,21]

All molecules investigated are alternant in nature. Analytical formulae are available for the energies of π-electron orbitals in polyacenes and cyclopolyacenes.[4–9]

Results and Discussion

After surveying the aromatic character of polyacenes, we analysed the %REs of cyclopolyacenes in some detail. Aromaticities of cyclopolyacenes are compared with those of polyacenes.

Linear Polyacenes.—The %REs of linear polyacenes are given in Table 1. For these molecules, the %RE rapidly decreases as the number of benzene rings (N) increases. The %RE of decacene ($N = 10$) is less than half that of benzene ($N = 1$). Linear polyacenes with $N \leqq 7$ have so far been prepared, higher members are too reactive to isolate under ordinary conditions.[22,23] Thus, the %REs of linear polyacenes are consistent with experiment.

For linear polyacenes, the SLE rapidly decreases as N

Table 1 TREs of linear polyacenes

N	TRE $(\vert\beta\vert)$	REPE $(\vert\beta\vert)$	%RE	SLE $(\vert\beta\vert)$	HOMO (β)
1	0.2726	0.0454	3.528	2.536	1.000
2	0.3888	0.0389	2.924	2.299	0.618
3	0.4746	0.0339	2.519	2.013	0.414
4	0.5531	0.0307	2.269	1.930	0.295
5	0.6298	0.0286	2.105	1.844	0.220
6	0.7063	0.0272	1.992	1.808	0.169
7	0.7828	0.0261	1.910	1.771	0.134
8	0.8595	0.0253	1.848	1.753	0.109
9	0.9361	0.0246	1.798	1.735	0.090
10	1.0129	0.0241	1.759	1.725	0.075
11	1.0897	0.0237	1.726	1.715	0.064
12	1.1665	0.0233	1.699	1.709	0.055
13	1.2433	0.0230	1.676	1.703	0.048
14	1.3202	0.0228	1.656	1.700	0.042
15	1.3970	0.0225	1.638	1.696	0.037

Table 2 TREs of zigzag polyacenes

N	TRE $(\vert\beta\vert)$	REPE $(\vert\beta\vert)$	%RE	SLE $(\vert\beta\vert)$	HOMO (β)
3	0.5459	0.0390	2.889	2.298	0.605
4	0.6884	0.0382	2.809	2.254	0.520
5	0.8348	0.0379	2.773	2.254	0.502
6	0.9795	0.0377	2.743	2.250	0.471
7	1.1247	0.0375	2.722	2.250	0.458
8	1.2697	0.0373	2.706	2.250	0.444
9	1.4147	0.0372	2.693	2.250	0.435
10	1.5597	0.0371	2.683	2.250	0.427
11	1.7046	0.0371	2.675	2.250	0.421
12	1.8496	0.0370	2.668	2.250	0.416
13	1.9946	0.0369	2.661	2.250	0.412
14	2.1397	0.0369	2.656	2.250	0.409
15	2.2845	0.0368	2.652	2.250	0.406

Table 3 TREs of linear cyclopolyacenes

N	TRE $(\vert\beta\vert)$	REPE $(\vert\beta\vert)$	%RE	SLE $(\vert\beta\vert)$	HOMO (β)
3	0.4788	0.0399	2.865	2.188	0.618
4	0.0349	0.0022	0.157	1.505	0.000
5	0.4276	0.0214	1.542	1.910	0.295
6	0.3637	0.0152	1.094	1.599	0.000
7	0.5339	0.0191	1.377	1.801	0.169
8	0.5695	0.0178	1.285	1.634	0.000
9	0.6773	0.0188	1.359	1.750	0.109
10	0.7422	0.0186	1.341	1.650	0.000
11	0.8304	0.0189	1.364	1.724	0.075
12	0.9042	0.0188	1.361	1.658	0.000
13	0.9856	0.0190	1.370	1.709	0.055
14	1.0621	0.0190	1.371	1.662	0.000
15	1.1411	0.0190	1.374	1.699	0.042

Table 4 TREs of zigzag cyclopolyacenes

N	TRE $(\vert\beta\vert)$	REPE $(\vert\beta\vert)$	%RE	SLE $(\vert\beta\vert)$	HOMO (β)
4	0.3336	0.0209	1.486	2.212	0.382
6	0.7994	0.0333	2.377	2.273	0.382
8	1.1374	0.0355	2.537	2.291	0.382
10	1.4422	0.0361	2.573	2.296	0.382
12	1.7371	0.0362	2.583	2.298	0.382
14	2.0287	0.0362	2.586	2.298	0.382

increases, so large species must be very reactive toward electrophiles and nucleophiles. The SLEs correspond to carbon atoms in the central benzene ring(s). The HOMO–LUMO energy separation also decreases rapidly as N increases. This again argues for less kinetic stability of larger linear polyacenes. Thus, both thermodynamic and kinetic stabilities are smaller for larger linear polyacenes.

Zigzag Polyacenes.—The TREs of zigzag polyacenes are given in Table 2. These molecules are highly aromatic with large positive %REs. The %RE is fairly constant for all zigzag polyacenes. Each zigzag polyacene is more aromatic than the linear isomer. Large %RE values of zigzag polyacenes are consistent with experiment. Zigzag polyacenes with $N \leqq 6$ have been prepared and are all very stable.[22,23]

The SLEs for zigzag polyacenes are fairly large compared with those for the linear isomers, indicating that the former species are much less reactive. The SLEs correspond to carbon atoms adjacent to the edge benzene rings. The HOMO–LUMO energy separation decreases very slowly as N increases. This also suggests that large zigzag polyacenes still have large kinetic stability. Note that a very stable graphite sheet has no HOMO–LUMO energy separation.[24] It is true that a very large π-electron system has no, or a very small, HOMO–LUMO energy gap even if it is thermodynamically very stable.

Linear Cyclopolyacenes.—The TREs of linear cyclopolyacenes are given in Table 3. Except for the first three members (N = 3, 4 and 5), the TRE increases very slowly as N increases. Therefore, the %REs of all these species are small, being comparable in magnitude to those of very reactive large linear polyacenes. Thus, sizeable linear cyclopolyacenes must be very reactive, rendering them possibly very difficult to prepare and handle compared with the partially hydrogenated derivatives.[1-3]

Except for the first three members, the SLEs are as small as those for the presumably very reactive large linear polyacenes, all being very small in harmony with the small %REs. The HOMO–LUMO energy separation vanishes when N is even or sufficiently large. This can be proved using an analytical formula for the π-electron energies.[5,8,9] These findings are consistent with the fact that none of the linear cyclopolyacenes have yet been prepared.

Zigzag Cyclopolyacenes.—Zigzag cyclopolyacenes necessarily consist of an even number of benzene rings. The TREs of these molecules are given in Table 4. As in the case of zigzag polyacenes, in general zigzag cyclopolyacenes have large %RE values. Therefore, these hydrocarbons are predicted to be as aromatic as zigzag polyacenes. Only cyclonaphthacene (N = 4) is exceptional, with a very small %RE.

The SLEs for zigzag cyclopolyacenes are as large as those for zigzag polyacenes. Therefore, both species are predicted to be chemically very stable. It should be possible to synthesize large zigzag cyclopolyacenes, if strain energy can be overcome. Interestingly, the HOMOs in all zigzag cyclopolyacenes lie at the same energy ($\alpha + 0.382\beta$), which can be proved using an analytical formula for the π-electron energies.[5,8,9] Therefore, all members have large HOMO–LUMO energy separations, suggesting that they are highly aromatic like typical planar polycyclic benzenoid hydrocarbons.

Kekulé Structure Counts.—For polycyclic benzenoid hydrocarbons including polyacenes, the TRE is roughly proportional to the logarithm of the Kekulé structure count.[25] For linear (lp) and zigzag (zp) polyacenes, the Kekulé structure counts are expressed in the form:[9]

$$K_{\mathrm{lp}}(N) = N + 1 \qquad (1)$$

$$K_{\mathrm{zp}}(N) = \frac{1}{\sqrt{5}}\left\{\left(\frac{1+\sqrt{5}}{2}\right)^{N+1} - \left(\frac{1-\sqrt{5}}{2}\right)^{N+1}\right\} \qquad (2)$$

For linear (lc) and zigzag (zc) cyclopolyacenes, the Kekulé structure counts are then given by

$$K_{\mathrm{lc}}(N) = 4 \qquad (3)$$

$$K_{\mathrm{zc}}(N) = K_{\mathrm{zp}}(N-1) + K_{\mathrm{zp}}(N-3) + 2 \qquad (4)$$

For linear isomers of polyacenes and cyclopolyacenes, the Kekulé structure count does not increase exponentially as N increases. Therefore, we might say again that these molecules are not highly aromatic. In contrast, for zigzag isomers of polyacenes and cyclopolyacenes, the logarithm of the Kekulé structure count is roughly proportional to N. This is consistent with the fairly constant %RE for these molecules. Thus, the Kekulé structure count is still useful for assessing aromatic character of cyclopolyacenes.

Clar Structures.—The aromatic character of a polycyclic benzenoid hydrocarbon can also be estimated qualitatively from its Clar structure. As illustrated in Fig. 2, a maximum number of isolated aromatic sextets are drawn in the Clar structure.[22,23] There is only one aromatic sextet in the Clar structure of any linear polyacene, and this is diluted in large linear polyacenes. Thus, as expected, the %REs of large linear cyclopolyacenes are small. There is no aromatic sextet in Clar structures of linear cyclopolyacenes with $N > 3$. This corresponds to the fact that these molecules are more or less olefinic and have small %REs.

Interestingly, two aromatic sextets can be chosen along the two peripheries of cyclanthracene ($N = 3$). This must be the reason that cyclanthracene alone has a large %RE. However, Haase and Zoeliner's MNDO calculation showed that cyclanthracene is not thermodynamically stable and would readily isomerize to a totally different structure.[10] In any case, highly strained cyclanthracene is not a realistic molecule.

There are $[(N + 1)/2]$ aromatic sextets in the Clar structure of zigzag polyacene formed by N benzene rings, where $[X]$ is the largest integer not larger than X. There are $[N/2]$ aromatic sextets in the Clar structure of zigzag cyclopolyacene formed by N benzene rings. For the two zigzag families, the number of aromatic sextets per ring is close to 1/2 when N is sufficiently large. This explains why these hydrocarbons have fairly constant %REs.

Hückel-like Rule for Cyclopolyacenes.—It is noteworthy that a Hückel-like rule is found in the %REs of linear cyclopolyacenes. For these molecules, the %RE and the SLE oscillate as N increases. Any linear cyclopolyacene with $2n$ benzene rings is slightly less aromatic than those with $2n - 1$ and $2n + 1$ benzene rings. This regularity is accompanied by the fact that linear cyclopolyacenes with $2n$ benzene rings have half-filled non-bonding π-electron orbitals. As Hückel pointed out in 1931,[26] chemical or kinetic instability is closely related to the existence of non-bonding orbitals. Note that anti-aromatic [4n]annulenes have half-filled non-bonding orbitals.[26]

Superaromaticity.—Extra stabilization may arise from macrocyclic conjugation along the cyclic array of benzene rings in cyclopolyacenes. This kind of stabilization energy may be called a superaromatic stabilization energy (SSE). We previously presented a graph-theoretical method for estimating the SSE,[27,28] which will not be repeated here. The SSE constitutes part of the TRE. Polyacenes have no SSEs by definition. In general, super-ring molecules have non-zero SSEs. The SSEs calculated for linear and zigzag cyclopolyacenes are listed in Table 5 and 6, respectively.

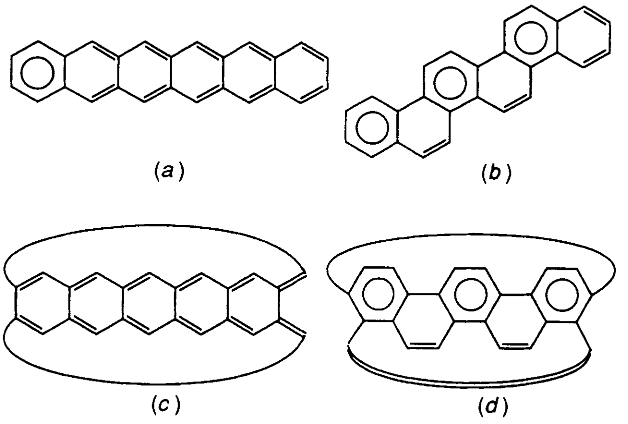

Fig. 2 Clar structures of (*a*) linear hexacene; (*b*) zigzag hexacene; (*c*) linear cyclohexacene and (*d*) zigzag cyclohexacene

Table 5 SSEs of linear cyclopolyacenes

N	TRE ($\lvert\beta\rvert$)	SSE ($\lvert\beta\rvert$)
3	0.4788	0.3841
4	0.0349	−0.1906
5	0.4276	0.1002
6	0.3637	−0.0544
7	0.5339	0.0302
8	0.5695	−0.0170
9	0.6773	0.0097
10	0.7422	−0.0055
11	0.8304	0.0032
12	0.9042	−0.0019
13	0.9856	0.0011
14	1.0621	−0.0006
15	1.1411	0.0004

Table 6 SSEs of zigzag cyclopolyacenes

N	TRE ($\lvert\beta\rvert$)	SSE ($\lvert\beta\rvert$)
4	0.3336	−0.2048
6	0.7994	−0.0601
8	1.1374	−0.0193
10	1.4422	−0.0065
12	1.7371	−0.0022
14	2.0287	−0.0008

As can be seen from Table 5, the SSEs of linear cyclopolyacenes oscillate about the value of zero. Linear cyclopolyacenes with an odd number of benzene rings are more or less superaromatic with positive SSEs, whereas those with an even number of benzene rings are more or less super-anti-aromatic with negative SSEs. The absolute value of the SSE decreases as N increases. Thus the oscillation of the SSE turned out to be the origin of the Hückel-like rule for linear cyclopolyacenes, and the high aromaticity in linear cycloanthracene ($N = 3$) can reasonably be attributed to high superaromaticity. Likewise, modest aromaticity in linear and zigzag cyclonaphthacene ($N = 4$) is attributable to high super-anti-aromaticity.

For linear cyclopolyacenes, a major part of the SSE must arise from the two peripheral conjugated circuits.[29,30] These circuits are the only conjugated circuits in these hydrocarbons. Peripheral circuits in linear cyclopolyacenes with an even number of benzene rings are anti-aromatic $4n$-membered ones, whereas those in the other linear cyclopolyacenes are aromatic $(4n + 2)$-membered ones. Therefore, it follows that the peripheral conjugated circuits are primarily responsible for the oscillation of the SSEs and then the Hückel-like rule.

As can be seen from Table 6, all zigzag cyclopolyacenes studied are more or less super-anti-aromatic in nature. All conjugated circuits associated with superaromaticity in zigzag cyclopolyacenes are anti-aromatic $4n$-membered ones. Zigzag cyclonaphthacene ($N = 4$) is highly super-anti-aromatic, and is much less aromatic than higher zigzag cyclopolyacenes. Whether they are linear or zigzag isomers, all realistic or sizeable cyclopolyacenes are almost free of superaromaticity.

Conclusions

All polyacenes and cyclopolyacenes proved to be more or less aromatic with different reactivities. They are aromatic in nature because they have no small $4n$-membered circuits.[29,30] Therefore, we believe that it will be possible to work with cyclopolyacenes under suitable conditions. Even highly anti-aromatic cyclobutadiene has been prepared.[31] Strain in a cyclopolyacene molecule is relaxed gradually as N increases, and sizeable cyclopolyacenes, such as linear cyclopentadecacacene ($N = 15$), may possibly be prepared in near future. Preparation of zigzag cyclopolyacenes is much more promising because of high aromaticity and low reactivity. It is noteworthy that the zigzag cyclodecacene conjugated system ($N = 10$) may be chosen from the equatorial part of fullerene-70.[32]

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