Aromaticity and Stability of Quinodimethanes

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Relatively large positive TREs for reactive non-Kekulé hydrocarbons, such as some quinodimethanes, were reasonably interpreted in terms of the extreme reactivity presumed for the polyene references.

Topological resonance energy (TRE) has been used widely and successfully as one of the energetic criteria for determining the degree of aromaticity.[1–3] It is a graph-theoretical variant of Hess–Schaad resonance energy.[4] The TRE concept can be applied to all π-systems that can be depicted in Hückel theory. Gutman, however, pointed out that the TRE values may be overestimated for non-Kekulé hydrocarbons.[5–7] Here, non-Kekulé hydrocarbons mean conjugated hydrocarbons for which classical Kekulé structures (i.e., closed-shell resonance structures) cannot be drawn. Thus, of three isomeric benzoquinodimethanes (**1**–**3**) presented in Fig. 1, the meta isomer [*m*-phenylenebis(methylene) **2**] has the largest positive TRE value although it is extremely reactive.[5,8] *m*-Phenylenebis(methylene) is nothing other than a non-Kekulé hydrocarbon classified as a biradical. It seemed that a large positive TRE value for a biradical is not consistent with its high reactivity.

As stated by Minkin et al.,[3] the apparent failure of the TRE scheme has attracted excessive attention for the simple reason that this method has been very extensively exploited for studying compounds of the most diverse types. The plain fact is that in most cases the TRE values are in quite satisfactory agreement with other estimates of aromaticity based on both theoretical and experimental approaches.[1–3] This is a very affirmative viewpoint that fully supports the TRE concept. Apart from this, we found that the above difficulty associated with a non-Kekulé hydrocarbon disappears if one takes into consideration the presumed chemical reactivity of the polyene reference used to estimate the TRE. In this short article, we show that, for non-Kekulé hydrocarbons, aromaticity does not always represent stability.

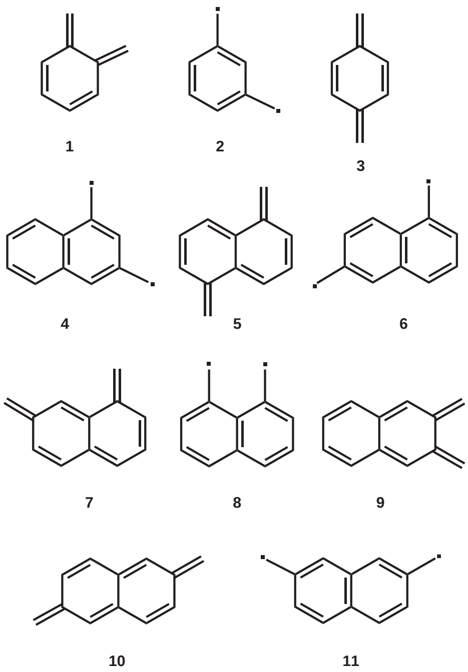

Fig. 1. Structural formulae for quinodimethanes.

TREs for the three phenylenebis(methylene) isomers (**1**–**3**) are listed in Table 1, together with related quantities. As can be seen from Fig. 1, isomers **1** and **3** (i.e., *o*- and *p*-phenylenebis(methylene) molecules) have singlet ground states. Isomer **2** [*m*-phenylenebis(methylene)] is a non-Kekulé open-shell biradical with a triplet ground state. Classical resonance structures can be written neither for **2** nor for the hypothetical polyene reference. Hence, **2** must be very reactive with biradicaloid character. This isomer is indeed extremely reactive.[8] In line with this, **2** has a pair of degenerate nonbonding molecular orbitals with no energy separation between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO). Furthermore, **2** has the smallest π-binding

Table 1. TREs and Related Quantities for Selected Quinodimethanes

Species	Total π-binding energy/$\lvert\beta\rvert$	HOMO–LUMO gap/$\lvert\beta\rvert$	TRE/$\lvert\beta\rvert$
o-Phenylenebis(methylene) (**1**)	9.954	0.590	0.059
m-Phenylenebis(methylene) (**2**)	9.431	0.000	0.096
p-Phenylenebis(methylene) (**3**)	9.925	0.622	0.061
1,3-Naphthoquinodimethane (**4**)	15.212	0.000	0.227
1,5-Naphthoquinodimethane (**5**)	15.561	0.323	0.151
1,6-Naphthoquinodimethane (**6**)	15.225	0.000	0.195
1,7-Naphthoquinodimethane (**7**)	15.522	0.344	0.142
1,8-Naphthoquinodimethane (**8**)	15.264	0.000	0.209
2,3-Naphthoquinodimethane (**9**)	15.532	0.339	0.141
2,6-Naphthoquinodimethane (**10**)	15.475	0.376	0.135
2,7-Naphthoquinodimethane (**11**)	15.170	0.000	0.183

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Fig. 2. Examples of non-Kekulé acyclic polyenes.

energy. It naturally follows that this isomer is not only thermodynamically but also kinetically unstable.

It is therefore noteworthy that *m*-phenylenebis(methylene) (**2**) has the largest positive TRE although it does not appear to be highly aromatic. We, however, must note that even a large positive TRE could not overcome the extreme reactivity presumed for a biradicaloid polyene reference. In other words, even if **2** had a much larger positive TRE, it would still be far from being large enough to overcome the extreme reactivity of the open-shell polyene reference. One should remember that even acyclic polyenes are diverse in chemical reactivity. Open-shell species are extremely reactive as compared with closed-shell acyclic polyenes, such as ethene and butadiene. Among such open-shell polyenes are trimethylenemethane (**12**) and tetramethyleneethane (**13**) in Fig. 2. Biradicaloid polyene references for cyclic biradicals must likewise be extremely reactive. Thus, the TRE should not be interpreted naively as an index of kinetic stability when the π-system and its polyene reference are open-shell species. Less aromatic ortho (**1**) and para (**3**) isomers are less reactive because they have closed-shell electronic configurations with non-zero HOMO–LUMO gaps.

In general, closed-shell acyclic polyenes exhibit marked bond-length alternation or double-bond fixation, with all π-electrons being formally assigned to individual CC double bonds.[3] Bond-length alternation lowers the energies of closed-shell acyclic polyenes and cyclic but olefinic hydrocarbons. However, cyclic biradicals, such as those presented in Fig. 1, never undergo marked bond-length alternation even if they are not highly aromatic. Likewise, their polyene references are supposed not to undergo marked bond-length alternation. Consequently, all π-electrons in such π-systems are forced to delocalize over the entire π-system, which must be why at least some biradicals give rise to large positive TREs.

Open-shell isomers of naphthoquinodimethane are also extremely reactive.[8] Eight isomers of naphthoquinodimethane **4**–**11** are added in Fig. 1. Four of them (**4**, **6**, **8**, and **11**) are non-Kekulé biradicals. Other isomers (**5**, **7**, **9**, and **10**) are closed-shell species. Isomers from which a conjugated circuit[9] can be chosen were not considered here because they are undoubtedly aromatic. It is again noteworthy that all open-shell isomers have smaller total π-binding energies and larger positive TREs than any closed-shell isomer. These open-shell isomers are again more aromatic than the closed-shell ones. All open-shell isomers have no HOMO–LUMO energy separation since they have a pair of degenerate nonbonding molecular orbitals. Therefore, we can safely say that these biradicals are moderately aromatic but not only thermodynamically but also kinetically very unstable. They have delocalized or mobile π-electrons since they cannot undergo double-bond fixation.

We have seen that for non-Kekulé hydrocarbons the TRE cannot be associated straightforwardly with the thermodynamic or kinetic stability of the π-system. As far as biradicaloid species are concerned, TRE is not correlative with chemical reactivity. However, the absence of such a correlation is never a flaw of the TRE concept. Chemical reactivity of a cyclic π-system reflects not only aromaticity but also the reactivity presumed for the polyene reference. Extreme reactivity of biradicaloid species should be attributed primarily to that of the polyene references, which cannot be overcome by the extra stabilization energy due to cyclic conjugation. It is still interesting to note that some cyclic biradicals are more aromatic than closed-shell isomers.

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