3454 © 1991 *The Chemical Society of Japan* NOTES *Bull. Chem. Soc. Jpn.*, ***64***, *3454—3456 (1991)* [Vol. 64, No. 11

Graph-Theoretical Analysis of the Cyclic Bicalicene Conjugated Systems

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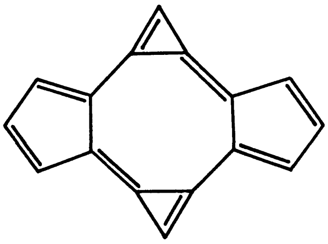
(Received June 5, 1991)

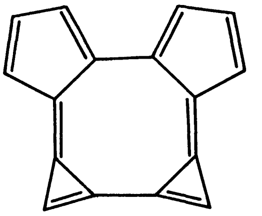
Synopsis. The so-called cyclic bicalicene is aromatic although it can be regarded as a perturbed [16]annulene. Graph-theoretical analysis shows that the aromaticity of this molecule arises primarily from three- and five-membered circuits and their combinations. The peripheral sixteen-membered circuit presumably destabilizes the conjugated system to a very slight extent.

In 1981 Yoshida and co-workers synthesized a novel pentacyclic conjugated hydrocarbon **1a**, and chose the appropriate name cyclic bicalicene for it.[1–5] It is stable in air at room temperature for several weeks. Its structural isomer in the form of **2a** has not been prepared yet. Since these two cyclic bicalicenes can be viewed as perturbed [16]annulenes, they are expected to be antiaromatic in nature. However, at least **1a** is aromatic in its chemical behavior.[2–5] Further, it exhibits neither strong first- nor second-order double-bond fixation.[6]

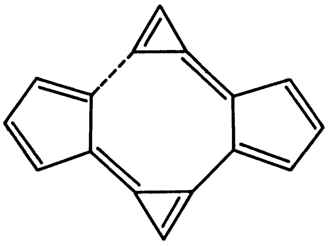
In general, aromaticity is associated straightforwardly with cyclic conjugation of π-electrons. All possible cyclic paths in a mono- or polycyclic conjugated system are responsible for aromaticity.[7–10] Such cyclic paths have been termed ring components or circuits in chemical graph theory.[7–10] Then, what kind of circuits contribute much to the aromaticity of **1a** and **2a**? In this paper, we make a graph-theoretical analysis of total π-electron energy for these cyclic bicalicenes, aiming at clarifying the role of peripheral conjugation. Hückel molecular orbital (HMO) theory is employed.



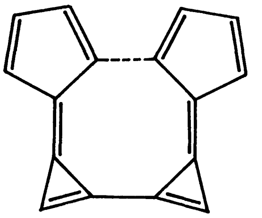
1a



2a



1b



2b

Results and Discussion

Not only the Dewar resonance energy (DRE) but also the topological resonance energy (TRE) has been used as a good index for determining the degree of aromaticity for cyclic conjugated systems.[7–12] The TREs defined by the simple Hückel model and the ω-technique (ω=1.4) will be denoted by TRE(ω=0) and TRE(ω=1.4), respectively. For alternant hydrocarbons the TRE(ω=0) is equal to the TRE(ω=1.4), whereas for non-alternant hydrocarbons the TRE(ω=1.4) is more or less smaller than the TRE(ω=0)., The TRE(ω=1.4) proved more realistic as an aromaticity index for non-alternant hydrocarbons such as cyclic bicalicenes **1a** and **2a**.[10]

The TREs of **1a**, **2a**, and related structures are listed in Table 1. There is no doubt about regarding **1a** as an aromatic species since both the TRE(ω=0) and the TRE(ω=1.4) are large and positive in sign. In contrast, **2a** has a smaller positive TRE(ω=0) and a negative TRE(ω=1.4), which suggest that this molecule is nonaromatic or antiaromatic in its chemical behavior. The DREs of **1a** and **2a** were calculated to be 15.75 and 6.71 kcal mol^{-1}, respectively. Here, the conjugated system of **1a** was assumed to be of D_{2h} symmetry. These DREs are fairly consistent with the corresponding TREs. For comparison, the TRE and the DRE for benzene are 0.273$|\beta|$[7,8] and 20.0 kcal mol^{-1},[12] respectively.

If Kekulé structures can be written for a subsystem of any cycle conjugated system, obtained by deleting a given circuit from the system, this very circuit is called a conjugated circuit. In 1976 Randić pointed out that the conjugated circuits are the main source of aromaticity in polycyclic aromatic molecules.[13,14] He successfully estimated the DREs of many polycyclic systems simply by enumerating every type of conjugated circuits.[13,14]

Table 1. Stabilization Energies (SEs) due to Type-II Circuits

Species	Total π-electron energy/β	SE/$\lvert\beta\rvert$	TRE/$\lvert\beta\rvert$
	A. Simple Hückel model (ω=0)		
1a	22.783	−0.020	0.657
1b	22.824	0.020	0.697
2a	22.599	−0.030	0.471
2b	22.659	0.030	0.531
	B. ω-Technique (ω=1.4)		
1a	22.319	−0.017	0.192
1b	22.352	0.017	0.226
2a	21.940	−0.030	−0.188
2b	22.000	0.030	−0.128

The peripheral sixteen-membered circuit is only one conjugated circuit in cyclic bicalicenes **1a** and **2a**. Accordingly, these molecules might be thought to be as antiaromatic as a sixteen-membered conjugated circuit. The DRE value estimated on this basis is −0.06 eV, which is obviously inconsistent with the positive DRE or TREs of **1a**.

Such an inconsistency can be settled by graph-theoretically analyzing the total π-electron energies of each cyclic bicalicene and its Möbius isomer. Here, a Möbius isomer is a hypothetical molecule, obtained by changing the sign of the resonance integral for one of the C–C bonds connecting the three- and five-membered rings in **1a**. A C–C bond with a resonance integral of $-\beta$ is identical with a twisted C–C bond because $-\beta$ usually represents a C–C bond twisted by $180°$.[15] Möbius isomers thus defined for **1a** and **2a** are given in **1b** and **2b**, respectively, in which dashed lines indicate twisted C–C bonds. Each has a Möbius-type peripheral conjugated subsystem.

Twenty circuits can be chosen from each cyclic bicalicene conjugated system. Eleven non-identical circuits in **1a** are presented in Fig. 1. Three- and five-membered circuits in **1a** and **2a** will be referred to as type-I circuits with all other ones referred to as type-II circuits. In Fig. 1, A and B are type-I circuits, while all others, including the peripheral conjugated circuit K, are type-II circuits. Type-I circuits in **1a** and **2a** are identical with those in **1b** and **2b**, respectively, whereas type-II circuits in each cyclic bicalicene become singly twisted in the Möbius isomer.

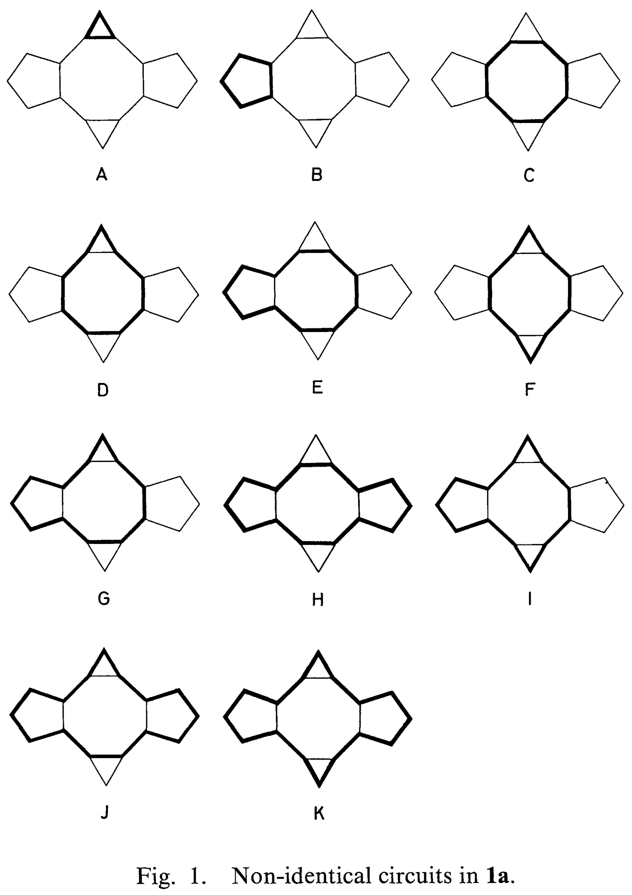


Fig. 1. Non-identical circuits in **1a**.

The total π-electron energy of a molecule can be expressed formally as a function of all circuits.[7-10,16] Some circuits lower the energy of the molecule, while others raise it. The former circuits are classified as aromatic circuits, and the latter ones as antiaromatic circuits. Every type-I circuit in **1a** and **2a** retains essentially the same aromatic character in **1b** and **2b**, respectively. However, aromatic and antiaromatic type-II circuits become antiaromatic and aromatic, respectively, on going from each cyclic bicalicene to its Möbius isomer.[17,18] Therefore, it follows that the energy difference between each cyclic bicalicene and the Möbius isomer represents the change in aromaticity of all type-II circuits.

HMO calculations revealed that each cyclic bicalicene and its Möbius isomer have similar total π-electron energies. For example, **1a** is less stable than **1b** only by $0.041|\beta|$. This fact indicates that type-II circuits, as a whole, destabilize **1a** to a very slight extent, and stabilize **1b** to a similar extent. Therefore, the stabilization energy (SE) of each cyclic bicalicene due to type-II circuits must be about half the energy difference between it and the Möbius isomer. The SE is about $-0.020|\beta|$ for **1a**, the negative sign of which indicates the predominant contribution of antiaromatic $4n$-membered type-II circuits. However, its absolute value is less than 10 percent of the TRE(ω=1.4). The same is essentially true of **2a**. In view of the very small SEs, it seems unlikely that peripheral conjugated subsystems in **1a** and **2a** have large annulenoid character.

It is worthy of note that **1a** has a large positive DRE and TRE although it does not have aromatic $(4n+2)$-membered conjugated circuits. It is type-I circuits such as three- and five-membered ones and their combinations that are important for characterizing electronic properties of **1a** and **2a**. These odd-membered circuits are never conjugated ones in Randić's sense.[13,14] His concept of conjugated circuits must somehow be modified in order to explain aromatic properties of cyclic bicalicenes.

Concluding Remarks

The Hückel $4n+2$ rule was originally proposed for monocyclic conjugated systems.[19] The idea that cyclic bicalicenes (**1a** and **2a**) may be regarded as perturbed [16]annulenes has been based on the unjustified assumption that this rule is applicable to polycyclic conjugated systems. We previously proved that the Hückel $4n+2$ rule in principle holds for monocyclic conjugated systems.[20] However, there is no reason to believe that annulenoid conjugation is important in such polycyclic conjugated systems as **1a** and **2a**. The peripheral conjugated subsystems in these species are so heavily perturbed that it is difficult to treat them naively as perturbed [16]annulenes. The present results are fully consistent with previous graph-theoretical considerations on **1a**.[2-5]

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