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Aromaticity of Butalene and Its Homologues

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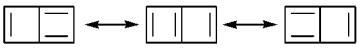
ABSTRACT

The aromaticity of a series of fused cyclobutadiene systems is discussed in terms of their resonance energies. While there is considerable variation in their resonance energies per π electron, all members of the series are calculated to be antiaromatic, though to a lesser degree than the parent cyclobutadiene.

Butalene (**1**) was first mentioned as a molecule of theoretical interest almost fifty years ago in the classic paper by Roberts, Streitwieser, and Regan in which they computed its Hückel



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delocalization energy (DE) to be 1.66β.[1] This high DE value apparently suggested to those authors that **1** might be isolable, since they noted that "Experiments directed toward simple derivatives of XII (butalene) are currently in progress." However, neither **1** nor any derivatives of **1** have been isolated, although Breslow reported trapping experiments of butalene and 2-methylbutalene which suggested that it might exist as a transient intermediate.[2]

Dewar calculated the barrier to ring opening of butalene to *p*-benzyne to be 4.6 kcal/mol with MINDO 3[3] and 3.0 kcal/mol with MNDO.[4] A number of ab initio calculations of **1** have also been reported, all of which predict butalene to be substantially higher in energy than *p*-benzyene.[5−7] More recently, a detailed study of the reaction pathway for the ring opening of butalene to *p*-benzyne predicted that it should proceed through a transition structure with D_2 symmetry with an activation energy of 5.9 kcal/mol.[8] Similar results were most recently reported by Warner and Jones.[9]

Although Roberts, Streitwieser, and Regan[1] calculated **1** to have a large DE, suggestive of aromaticity, more modern methods of computing resonance energies, using the Dewar reference structure,[10] have found it to be antiaromatic. Dewar, Kohn, and Trinajstić reported[11] a RE of −6.5 kcal/mol based on a "π approximation," and we found[12] its Hückel resonance energy per π electron (REPE) to be −0.067β. Both the ab initio results and the newer calculated resonance energies of **1** are in agreement with the failure to isolate the compound.

REPE applies the simple Hückel MO method in which π-overlap between all bonded carbons is taken to be the same ($\beta = 1$). Hence, the REPE is calculated for the form of butalene which has two "joined squares", similar to cyclobutadiene's REPE being computed for square cyclobutadiene. If a system is calculated to have a large negative REPE (antiaromatic), it will presumably undergo distortions to decrease the conjugation of its π electrons. Cyclobutadiene has been shown both experimentally[13] and theoretically[14] to

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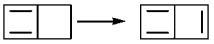
exist as a rectangle rather than a square with unusually long sp^2-sp^2 C−C bonds. However, ab initio calculations indicate that this distortion is not enough to completely remove the antiaromaticity of cyclobutadiene.[15]

On the basis of its REPE, butalene would be expected to undergo a similar distortion by elongation of the central bond to lower its antiaromaticity. This would diminish the overlap between p-orbitals on these carbons, leading in the extreme case to *p*-benzyne. Such a distortion not only would diminish the antiaromaticity of butalene but would also gain the aromatic stabilization of the benzene system. Another driving force for this distortion is the relief of strain. This gain in stabilization of course is offset by the loss of a σ-bond. DFT calculations indeed indicate that this central bond in **1** is predicted to be unusually long.[8,9] The question then arises whether the elongation of this bond is sufficient to remove the antiaromaticity of butalene.

Recently Warner and Jones concluded from "double bond stablization energies" obtained with DFT calculations for an isodesmic reaction that **1** might be aromatic.[9] This conclusion was based on their finding that the introduction of a second bond into cyclobutene to give cyclobutadiene was endothermic by 32.1 kcal/mol, while the introduction of the third double bond into bicyclo[2.2.0]hexa-1,3-diene (**2**) to give butalene was exothermic by −18.6 kcal/mol. In the isodesmic reactions of Warner and Jones, the introduction of a second double bond into cyclobutene to form cyclobutadiene clearly supports the antiaromaticty of cyclobutadiene. However, the introduction of the third double bond into dihydrobutalene (**2**), while forming butalene, "destroys" the very antiaromatic



cyclobutadiene system present in **2**. Warner and Jones' finding that this is an exothermic process is in agreement with the REPE results, since REPE's predict butalene to be significantly less antiaromatic than cyclobutadiene. As suggested by Warner and Jones, the elongation of the central C−C bond might be enough to "remove" the antiaromaticty of the butalene system.

Warner and Jones also addressed the aromaticity of the higher homologues of butalene, **3** and **4**. Since REPE had not been previously calculated for these, they are given below in Table 1 for **3** and **4** as well as for the larger condensed cyclobutadienes, **5**−**10**. Examination of this table shows that the behavior of this series is very different from that of the linear benzenoid hydrocarbons (benzene, naphthalene, anthracene...).[16] While the benzenoid series begins with the very aromatic benzene molecule and the aromaticity of the following members of the series steadily decreases, this series (cyclobutadiene, **1**, **3**, **4**, **5**...) begins with the very antiaromatic cyclobutadiene, but it does not continue with a steady decrease in antiaromaticity.

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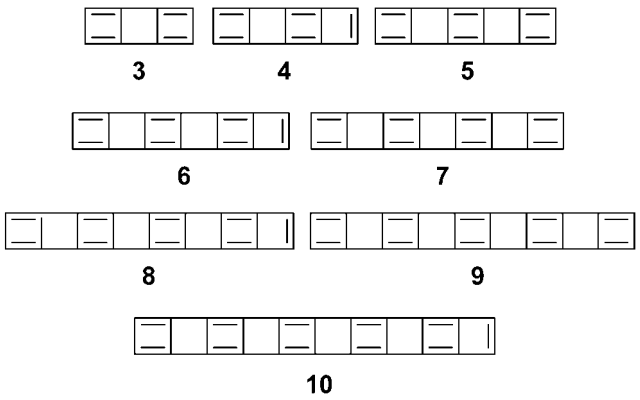
Table 1. Total Dewar Resonance Energies (TRE) and Resonance Energies per π Electron (REPE) in Units of β for Compounds **1** and **3**−**10**

compound	RE	REPE
cyclobutadiene	−1.07	−0.268
1	−0.40	−0.067
3	−0.63	−0.079
4	−1.22	−0.122
5	−1.00	−0.083
6	−1.19	−0.085
7	−1.63	−0.102
8	−1.53	−0.085
9	−1.72	−0.086
10	−2.09	−0.095

One interesting aspect of these results is that after cyclobutadiene every third compound in the table (**4**, **7**, and **10**) is significantly more antiaromatic than either of the two preceding compounds. At first this appears to be a puzzle, but examination of the Hückel energy levels shows that cyclobutadiene, **4**, **7**, and **10** are predicted, like cyclobutadiene, to be open shell systems (the highest occupied level with energy equal to zero is degenerate). Focus here will be on compounds **1**, **3**, and **4** for which Warner and Jones have reported DFT computational results.



As mentioned above, butalene (**1**) while predicted to be antiaromatic is significantly less antiaromatic than cyclobutadiene. Compound **3** is predicted to be slightly more antiaromatic than butalene. Warner and Jones found the compound to deviate significantly from planarity in DFT calculations.[9] This suggests that the compound prefers to limit its conjugation, again indicative of antiaromaticity. Compound **4** is predicted to be significantly more antiaromatic than either **1** or **3**. Hence there should be a strong driving force to minimize its conjugation. In agreement with this is its highly nonplanar structure predicted by DFT calculations.[9] Its U-shaped structure is reminiscent of that of cyclooctatetraene, another strongly antiaromatic system.

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