

## The Aromaticity of Annulenoannulenes

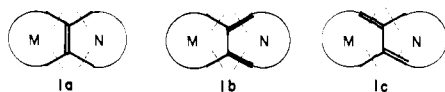
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**Abstract:** The aromatic character of the annulenoannulenes has been examined theoretically and has been found to be dominated by the aromaticity of the two fused rings rather than by that of the molecular periphery.

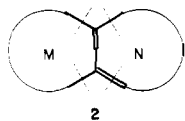
The chemistry of annulenes has received considerable attention over the past decade, and it is apparent from a recent symposium<sup>2</sup> that there is now major interest in the related annulenoannulenes. An annulenoannulene results from the fusion of two annulene rings to form a  $\pi$  system with one or more bonds in common. We shall examine here the predicted aromaticity of these systems and consider in particular whether this aromaticity approximates either that of the molecular periphery or the average aromaticity of the fused rings.

An annulene is a completely conjugated cyclic hydrocarbon with an even number of carbon atoms. An  $[M]$ annuleno $[N]$ -annulene<sup>3</sup> must therefore have an even number of carbon atoms in each of the fused rings. To show that this implies that the number of bonds shared by the fused rings must be odd, consider first cutting a fragment out of the interior of a polyene chain. If the two bonds cut are either both double or both single, the fragment removed contains an even number of carbon atoms. If one cut bond is single and the other double, the fragment has an odd number of carbons. Possible resonance structures for the central portion of an  $[M]$ annuleno $[N]$ annulene with one shared bond are indicated in **1a-c**. Structure **1a** is unique, but both **1b** and **1c** are one of a pair, the other



member of which is obtained by switching the double bonds shown to the opposite ring. By the reasoning above, the dotted lines cut off even carbon fragments in the rings of **1a** and **1b** but odd fragments in **1c**. The two rings in **1c** are therefore not even membered and hence **1c** cannot be a resonance structure of an annulenoannulene. The same applies to annulenoannulenes with 3, 5, 7, . . . , shared bonds; all will have the three resonance structures indicated by **1a** and **1b**.

There are four possible resonance structures for an annulenoannulene with two shared bonds. One of these is shown in **2**, another is obtained by interchanging the top and bottom



halves of **2**, and the others are obtained by moving the double bond in these two into the opposite ring. In **2**, the fragment in the  $m$  ring cut off by the dotted lines is even;  $m$  is therefore odd and **2** is not an annulenoannulene. The same holds for the other three resonance structures and for cases of 4, 6, 8, . . . , shared bonds. Annulenoannulenes must therefore share an odd number of bonds.

Let  $n = 2k + 1$ ,  $k = 0, 1, 2, \dots$ , be the number of shared bonds in an  $[M]$ annuleno $[N]$ annulene. The total number of carbon atoms in the system is then  $N + M - (n + 1)$ , and the number in the peripheral ring is  $N + M - 2n$ . Using the term "Hückel" for rings with  $4i + 2$  atoms ( $i = 1, 2, \dots$ ) and

"anti-Hückel" for those with  $4i$ , it is useful to distinguish three classes of annulenoannulenes: (1) Hückel rings of  $M = 2i + 2$  atoms fused to Hückel rings of  $N = 4j + 2$  atoms give a Hückel periphery of  $4(i + j - k) + 2$ ; (2) anti-Hückel rings of  $4i$  atoms fused to another of  $4j$  atoms give a Hückel periphery of  $4(i + j - k - 1) + 2$ ; (3) Hückel rings of  $4i + 2$  fused to anti-Hückel rings of  $4j$  give an anti-Hückel periphery of  $4(i + j - k)$  atoms. For example, the fusion of two benzene rings leads to naphthalene, a  $10\pi$  system, and the fusion of two cyclooctatetraene rings gives octalene, a  $14\pi$  system. The latter has been considered a potentially aromatic molecule since it contains a Hückel periphery.<sup>4</sup> This conclusion however was based in part on the application of Hückel's rule to a bicyclic system although the rule was derived only for monocyclic hydrocarbons. Roberts<sup>5</sup> had noted earlier the lack of theoretical justification for the application of Hückel's rule to other than monocyclic hydrocarbons. Breslow<sup>6</sup> again raised the question of the aromaticity of octalene in 1965 but left it open. Other earlier predictions of the aromaticity of annulenoannulenes were based on Hückel delocalization energies which have been shown to be unreliable.<sup>7,8</sup> Recent advances in the theoretical treatment of cyclic conjugated systems now allow the prediction of aromatic character with reasonable confidence.<sup>7-14</sup> We shall report predicted aromaticities of annulenoannulenes based on several of these methods.

Consider first systems of type (1) and type (2) in which two rings of equal size are fused with one shared bond to give  $[N]$ annuleno $[N]$ annulenes. The resonance energies per  $\pi$  electron of examples of these systems are listed in Table I, and Figure 1 shows that they exhibit an initial strong alternation between aromaticity and antiaromaticity which moderates with increasing ring size in much the same way as for the annulenes themselves.<sup>15</sup>

For comparison, we have also applied the graph theoretical method of Trinajstić<sup>11</sup> and Aihara<sup>12</sup> to the annulenoannulenes. Figure 2 shows a comparison of the graph theoretical REPE with that computed by our method. There is some scatter, but the two methods do correlate to within the estimated error ( $\pm 0.005\beta$ ) of our method.<sup>8b</sup> The best line for the aromatic systems appears slightly different from that for the antiaromatics, but the accuracy of the correlation is not sufficient to say whether this is significant. The curve does not pass through the origin, and this is probably connected to the fact that our REPE tends to  $+0.005\beta$  rather than exactly to 0 for the infinite annulene and for the infinite polyene chain.<sup>15</sup>

The graph theoretical method does not require the bond energy parameters that we need to apply our method; hence it is more easily generalizable to any class of heterosystem. Perhaps an even more significant advantage of the graph theoretical method is that it can treat ions and radicals to which we have not yet seen how to apply our method. The crucial difference between the two methods lies in the reference structure to which a given molecule is compared. In the graph theoretical treatment this is such that all acyclic systems are defined to have exactly zero resonance energy. Such a defini-

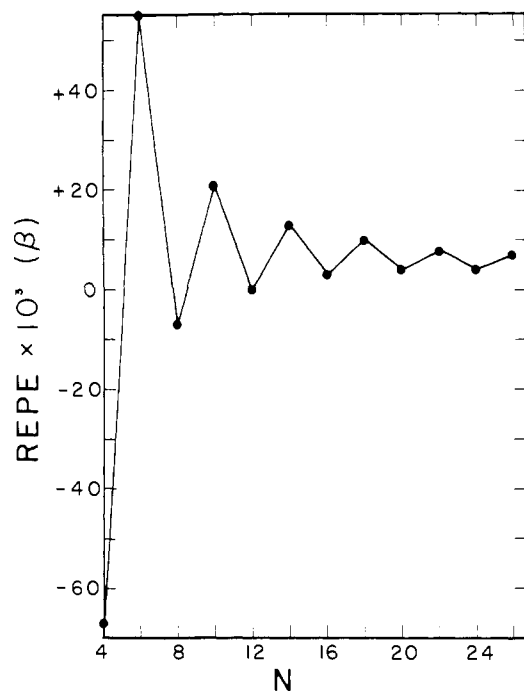


Figure 1. Resonance energy per  $\pi$  electron of  $[N]$ annuleno $[N]$ annulenes.

Table I. Resonance Energies per  $\pi$  Electron (REPE) of the  $[N]$ -Annuleno $[N]$ annulenes with One Shared Central Bond

$N$	REPE ( $\beta$ )	$N$	REPE ( $\beta$ )
4	-0.067	18	+0.010
6	+0.055	20	+0.004
8	-0.007	22	+0.009
10	+0.021	24	+0.005
12	0.001	26	+0.008
14	+0.013	28	+0.005
16	+0.003	30	+0.007

tion automatically precludes Gund's concept of "Y aromaticity".<sup>16</sup> On the other hand, Dewar's reference structure,<sup>9</sup> which we use in slightly modified form,<sup>8a</sup> makes use of the bond energy additivity of acyclic polyene hydrocarbons. Other acyclics will not necessarily show this additivity (in fact in some unpublished calculations we find that some, especially those with carbon-nitrogen bonds, do not) and hence may be Y aromatic. Whether the graph theoretical or the additive reference has clear advantages over the other for the experimental chemist remains to be seen.

One practical difficulty we have encountered in applying the graph theoretical (GT) method is that as the size of the molecule increases, the number of Sach's graphs increases factorially leading to a very lengthy computation. For example, the computation of the GT resonance energy of [16]annuleno[16]annulene required 10.5 min of CPU time on a DEC 1099 system. [18]Annuleno[18]annulene was not completed after approximately 30 min. This may be compared with CPU times of 1.3 and 2.0 required to compute the REPE's by our method. A better way of counting the Sach's graphs might improve the GT computing times, but, because of the long times required with our program, not all the larger annulenoannulenes were examined by graph theory, and the number of points in Figure 2 is not equal the number of our REPE's listed in Tables I-III.

The aromaticity of two fused Hückel rings is no great surprise, but a question that has been raised is whether the re-

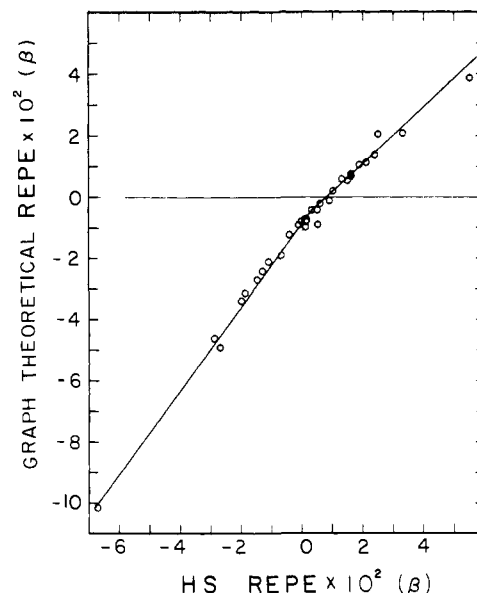


Figure 2. A comparison of Hess-Schaad with Trinajstić-Aihara (graph theoretical) REPE.

Table II. Resonance Energies per  $\pi$  Electron (REPE) of the  $[N]$ -Annuleno $[M]$ annulenes with One Shared Central Bond

$N$	$M$	REPE ( $\beta$ )	$N$	$M$	REPE ( $\beta$ )
4	6	-0.027	6	24	+0.010
4	8	-0.029	6	26	+0.015
4	10	-0.020	6	28	+0.010
4	12	-0.019	6	30	+0.013
4	14	-0.015	8	10	+0.001
4	16	-0.013	8	12	-0.003
4	18	-0.011	8	14	0.000
6	8	+0.005	8	16	-0.001
6	10	+0.033	8	18	+0.001
6	12	+0.009	10	12	+0.005
6	14	+0.024	10	14	+0.016
6	16	+0.010	10	16	+0.006
6	18	+0.019	10	18	+0.014
6	20	+0.010	10	20	+0.007
6	22	+0.017			

sultant annulenoannulene would be closer in aromaticity to that of the individual rings or to that of the periphery.<sup>6,17</sup> Our calculations predict the former. For example, naphthalene with REPE = +0.055 $\beta$  is closer to benzene (REPE = +0.065 $\beta$ ) than to its periphery of [10]annulene (REPE = +0.026 $\beta$ ). [10]Annuleno[10]annulene with a periphery of 18 electrons has an REPE of +0.021 $\beta$  and is calculated to be more like [10]annulene (REPE = +0.026 $\beta$ ) than like [18]annulene (REPE = +0.012 $\beta$ ).

The fusion of two anti-Hückel rings is clearly predicted to give systems that will not be aromatic in spite of their Hückel peripheries. Butalene is calculated to be strongly antiaromatic, and this appears to be borne out experimentally in that all attempts to isolate butalene have failed.<sup>18,19</sup> Octalene with an REPE of -0.007 $\beta$  is in the borderline region between antiaromatic and aromatic.<sup>20</sup> Breslow<sup>21</sup> reported the synthesis of benzo[*c*]octalene in 1966 and concluded that the eight-membered rings have tub conformation. The synthesis of octalene itself was reported only last year by Vogel.<sup>22</sup> He characterized octalene as a very reactive polyolefin which is in excellent agreement with our calculated REPE. The GT REPE is -0.019 $\beta$  which suggests octalene should be antiaromatic. This is not necessarily in disagreement with experiment since NMR evidence<sup>23</sup> indicates that octalene is a nonplanar mol-

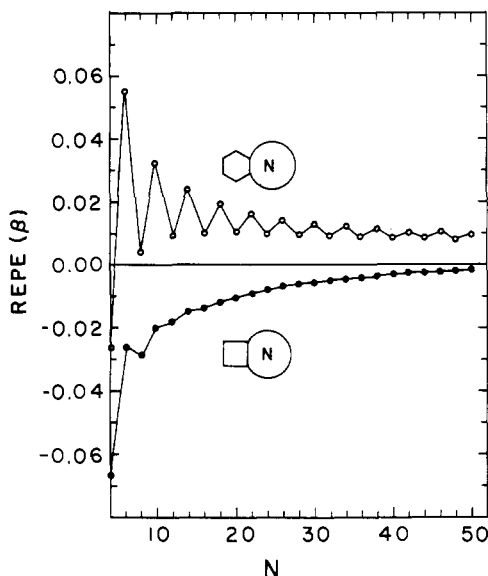


Figure 3. Resonance energy per  $\pi$  electron of [4]annuleno[ $N$ ]annulenes and of [6]annuleno[ $N$ ]annulenes.

Table III. Resonance Energies per  $\pi$  Electron (REPE) of [ $N$ ]-Annuleno[ $M$ ]annulenes with Three and Five Shared Bonds

$N$	$M$	no. of central bonds	REPE ( $\beta$ )
10	10	3	0.025
12	12	3	0.001
14	14	3	0.015
16	16	3	0.003
18	18	3	0.011
20	20	3	0.004
22	22	3	0.009
24	24	3	0.005
26	26	3	0.008
28	28	3	0.005
30	30	3	0.007
14	14	5	0.016
16	16	5	0.003
18	18	5	0.011
20	20	5	0.004
22	22	5	0.009
24	24	5	0.005
26	26	5	0.008
28	28	5	0.005
30	30	5	0.007
14	16	3	0.005
14	18	3	0.012
14	20	3	0.006
14	22	3	0.011
16	18	3	0.005
16	20	3	0.004
16	22	3	0.005
16	24	3	0.004
16	18	5	0.004
16	20	5	0.004
16	22	5	0.004
16	24	5	0.004
18	20	5	0.005
18	22	5	0.010
18	24	5	0.006
18	26	5	0.009

ecule and the calculation was performed assuming a planar system. This is similar to the case of cyclooctatetraene. Both methods predict it to be strongly antiaromatic but yet it is a stable, isolable compound presumably due to its tub conformation in which the p orbitals are very nearly orthogonal.

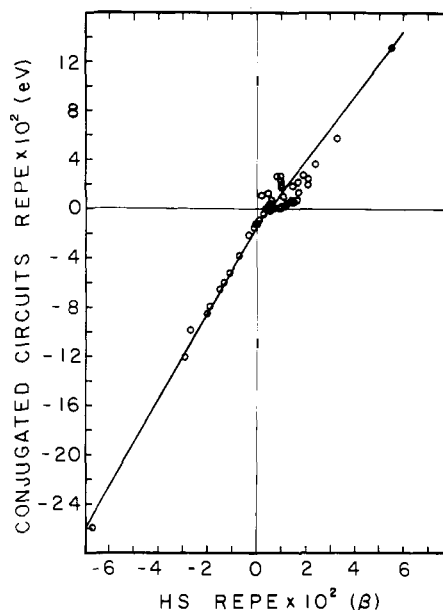


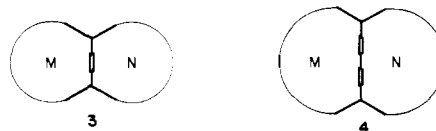
Figure 4. A comparison of Hess-Schaad REPE with that of Randić's conjugated circuits method.

The larger systems containing two anti-Hückel rings are all predicted by both methods to be essentially nonaromatic. Hence, the proposal that two anti-Hückel rings fused might yield an aromatic system has now been shown to be invalid by both theory and experiment.

In order to obtain a system of type (3) two rings of differing size are required. The resonance energies of a number of examples of this type are listed in Table II. With the exception of those compounds in which one of the rings is a cyclobutadiene the fusion of an anti-Hückel ring to a Hückel ring leads to systems which are either nonaromatic or border on the nonaromatic region. The cyclobutadiene systems listed all seem to be antiaromatic. They, along with the benzannulenes, are plotted in Figure 3. The smallest member, benzocyclobutadiene, is strongly antiaromatic in agreement with its known experimental properties.<sup>24</sup> Several other systems of type (3) are known; derivatives of benzocyclooctatetraene,<sup>25</sup> [14]-annuleno[16]annulene,<sup>3</sup> benzo[20]annulene,<sup>26a</sup> benzo[16]-annulene,<sup>26a</sup> and benzo[12]annulene.<sup>26b</sup>

Also included in Table II are [ $N$ ]annuleno[ $M$ ]annulenes (i.e., the two rings are of different size) which are of types (1) and (2). Their behavior is predicted to be analogous to the corresponding type of the [ $N$ ]annuleno[ $N$ ]annulenes; i.e., fusion of two Hückel rings leads to an aromatic system whereas fusion of two anti-Hückel systems generally yields a nonaromatic system except when cyclobutadiene is one of the rings. Sondheimer has recently reported the preparation of [4]annuleno[16]annulene and its REPE of  $-0.013\beta$  is in good agreement with its experimental behavior (polymerizes rapidly on formation).<sup>27</sup> He has also prepared several derivatives of the benzannulenes listed in Table II: benzo[14]-<sup>28</sup> and benzo[18]annulene.<sup>26</sup> The parent benzo[14]annulene has been synthesized by Staab.<sup>29</sup>

Finally we have considered the annulenoannulenes which contain three or five common bonds (3 and 4). As shown above,



the same three types exist as in the case of one common bond. In Table III are listed our results for selected systems of 3 and

4. A comparison of the REPE's of these annulenoannulenes with the analogous systems in Tables I and II indicates that the dominant feature in determining their aromaticity is again the size of the two fused rings. For example REPE values of [18]annuleno[18]annulenes with one, three, and five common bonds are  $+0.010\beta$ ,  $+0.011\beta$ , and  $0.011\beta$ , respectively. The aromaticity of annulenoannulenes with three common bonds has been shown by Nakagawa by the synthesis of dehydro derivatives of the [14][14],<sup>30</sup> [18][18],<sup>31</sup> [14][18],<sup>32</sup> and [14][22]<sup>33</sup> systems. Nakagawa's NMR data for the [14][14] system<sup>30</sup> when compared to that of his [14]annulene<sup>34</sup> and [22]annulene<sup>35</sup> derivatives show that the [14][14] molecule (REPE =  $+0.015\beta$ ) is closer in aromaticity to [14]annulene (REPE =  $+0.016\beta$ ) than to [22]annulene (REPE =  $+0.010\beta$ ),<sup>36</sup> in agreement with our predictions. A single example has been reported of an annulenoannulene containing five central bonds. Nakagawa has prepared a dehydro[18]-annuleno[18]annulene which contains two 18-membered rings fused by five central bonds.<sup>37</sup>

Our main conclusion that the aromaticity of all annulenoannulenes is determined by the nature of the fused rings rather than by the size of the periphery is also predicted nicely by Randić's method of conjugated circuits.<sup>13</sup> All annulenoannulenes have three resonance structures: that of **1a** and the pair corresponding to **1c**. **1a** contains conjugated circuits of size  $M$  and  $N$ , but not a circuit around the molecular periphery. Both of the resonance structures **1b** contain peripheral circuits of size  $M + N - 2n$  ( $n$  = number of common bonds); one also has a circuit of  $M$  and the other of  $N$  atoms. By Randić's method the resonance energy per  $\pi$  electron is then  $2[f_M + f_N + f_{M+N-2n}]/3(M + N - n - 1)$  for an  $[M]$ annuleno[ $N$ ]annulene with  $n$  common bonds. Here the  $f_i$ 's are contributions of the individual circuits which in Randić's notation are  $R_i = f_{4i+2}$ ,  $Q_i = f_{4i}$  ( $i = 1, 2, 3, \dots$ ). The peripheral contribution  $f_{M+N-2n}$  is usually negligible (butalene and the highly strained cases of many shared bonds between small fused rings provide exceptions) compared to those of the fused  $M$  and  $N$  rings. Hence our result. Figure 4 shows a fair correlation between our REPE and that computed by Randić's method.

## References and Notes

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- (2) The Third International Symposium on Novel Aromatic Compounds (ISNA3), sponsored by the Division of Organic Chemistry, American Chemical Society, San Francisco, August 22-26, 1977.
- (3) We have adopted the nomenclature proposed by T. M. Cresp and F. Sondheimer, *J. Am. Chem. Soc.*, **99**, 194 (1977).
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