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AROMATICITY OF NON-ALTERNANT ANNULENOANNULENES AND OF CORANNULENES

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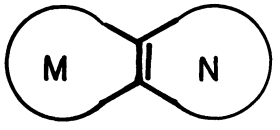
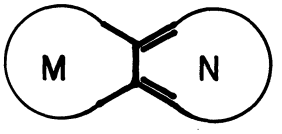
Abstract - Resonance energies of non-alternant annulenoannulenes and corannulenes have been calculated. The aromatic character of the former appears to be dominated by their periphery, in contrast to the behavior of the alternant annulenoannulenes. For the corannulenes no simple systematic behavior is apparent. Kekulene and many compounds of similar structure are predicted to be aromatic regardless of their inner and outer peripheral circuits.

NON-ALTERNANT ANNULENOANNULENES

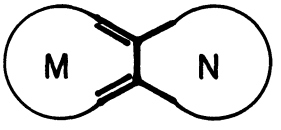
Annulenoannulenes are currently one of the major topics of interest and activity in the field of nonbenzenoid aromatic chemistry (Ref. 1). An annulenoannulene may result from the fusion of two annulene rings to form a π system with one or more bonds in common (Ref. 2). A neutral annulene is a completely conjugated cyclic hydrocarbon with an even number of carbon atoms. On the other hand, annulenoannulenes need not necessarily have an even number of carbon atoms in each of the fused rings. Hence, a classification into alternant annulenoannulenes and nonalternant annulenoannulenes may be appropriate. The latter are made up of two fused odd-membered rings. The alternant annulenoannulenes have three Kekulé resonance structures. These are indicated in 1a-c for the central part of an alternant [M]annuleno[N]annulene with one shared bond.



1a



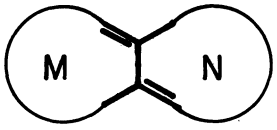
1b



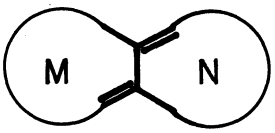
1c

Structure 1a is unique, but 1b and 1c are a pair, which are interconverted by switching double bonds shown to the opposite ring.

The number of Kekulé resonance structures of a nonalternant annulenoannulene is limited to two which interchange the single and double bonds of the periphery. These are indicated in 2a-b for the central part of a nonalternant [M]annuleno[N]annulene.

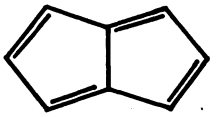


2a



2b

We have recently reported our results on resonance energy calculations of alternant annulenoannulenes (Ref. 3) and concluded that the aromatic character of these systems is dominated by the aromaticity of the two fused rings rather than by that of the molecular periphery. Here we shall consider the aromaticity of nonalternant annulenoannulenes. An example of such a system is pentalene (3) with two fused five-membered rings.



3

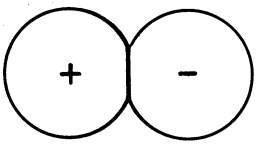
The central bond remains single in both Kekulé structures of the nonalternant annulenoannulenes whereas in the alternants it is double in one of the three Kekulé structures. This suggests that that the aromaticity of the nonalternant annulenoannulenes might be similar to that of the peripheral annulene, in direct contrast to the behavior of the alterant annulenoannulenes.

We propose to adopt the nomenclature of Sondheimer (Ref. 2) for the nonalternant annulenoannulenes. Thus in the name [M]annuleno[N]annulene M and N will specify the size of the two odd-membered rings, for example, pentalene will be [5]annuleno[5]annulene. In Table 1 nonalternant annulenoannulenes are compared with the corresponding peripheral annulenes.

Table 1. Resonance energies per π electron (REPE) of the nonalternant [N]annuleno[M]annulenes with one shared central bond compared with the [P]annulenes of the same number of π electrons

annulenoannulenes			annulenes	
N	M	REPE(β)	P	REPE(β)
3	3	-0.100	4	-0.268
3	5	+0.055	6	+0.065
5	5	-0.018	8	-0.060
3	7	-0.016	8	-0.060
3	9	+0.025	10	+0.016
5	7	+0.023	10	+0.016
7	7	-0.004	12	-0.011
5	9	-0.004	12	-0.011
5	11	+0.015	14	+0.012
7	9	+0.015	14	+0.012
9	9	0.000	16	-0.006
5	13	+0.001	16	-0.006
7	11	0.000	16	-0.006
9	11	+0.011	18	+0.010
11	11	0.000	20	-0.005
11	13	+0.009	22	0.010
13	13	+0.002	24	-0.002

One sees immediately that the periphery of these annulenoannulenes does dominate their aromaticity. Those with a 4n + 2 periphery are predicted to be aromatic and those with a 4n periphery antiaromatic. This is consistent also with the contribution of the dipolar [M]annulenium[N]annulenide structure (2c) in which the two components are complementary aromatic Hückel ions.



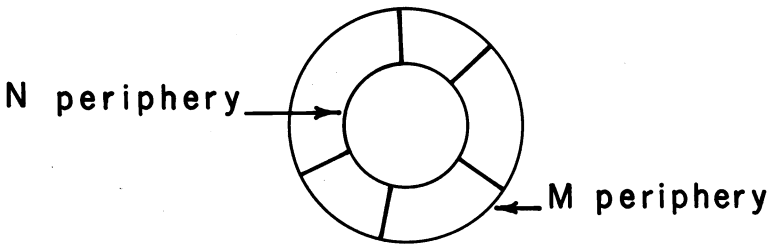
2c

For smaller rings, the nonalternant annulenoannulenes oscillate between antiaromatic and aromatic, like, but not as strongly as, the corresponding annulenes, and then moderate toward nonaromatic with increasing ring size. The methods of Randić (Refs. 4 & 5) and of Herndon (Ref. 6) would also predict this general behavior, though both would predict the aromaticity of a nonalternant annulenoannulene exactly equal to that of the peripheral annulene.

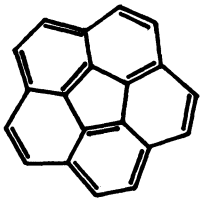
Experimental results appear to support the predictions for those systems which are known in Table 1. While the highly strained 1,3-dehydrobenzene ([3],[5]) is unknown there is evidence that it does have significant aromatic stabilization (Refs. 7 & 8). Pentalene ([5],[5]) has been found to be a very unstable molecule (Refs. 9 & 10). The aromaticity of azulene ([5],[7]) has been well documented, and heptalene ([7],[7]) has been characterized as a reactive polyene (Ref. 11). The only other known system in Table 1 is a derivative of [5]annuleno[9]annulene recently reported by Hafner (Ref. 12). An x-ray analysis indicates that the nine-membered ring is tub-shaped like that of cyclooctatetraene.

CORANNULENES

The recent synthesis of kekulene by Staab (Ref. 13) has brought about a renewed interest in corannulenes. The trivial name corannulene was originally coined by Lawton for compound 4 (below). Lawton's corannulene is a nonalternant system built of an inner 5-membered peripheral circuit and outer 15-membered peripheral circuit. In this system, the contribution of the aromatic dipolar structure in which both the inner and the outer peripheral circuits attain Hückel "aromaticity" has been considered. Corannulenes were originally defined by Hellwinkel as polycyclic hydrocarbons "possessing an inner annulene system which is connected over all its radial valences with an outer annulene system" (Ref. 15). For example one can consider coronene as a corannulene containing an inner [6]annulene system and an outer [18]annulene ring. Hellwinkel proposed a nomenclature for corannulenes based on the inner and outer ring sizes. However we also wish to consider compounds such as 7 (below) in which not every inner carbon is bound directly to an outer carbon atom. We therefore propose a modification of Hellwinkel's nomenclature. After the word corannulene is a string of superscripted numbers in square brackets. These specify the size of the small rings which are linked to form the corannulene. The superscript gives the number of carbon atoms in the specified small ring, lying in the outer periphery of the corannulene and unshared by neighboring rings. Hence coronene would have a string of six sixes each with a superscript of 2. Compounds 4-22 are all named in this manner. While Hellwinkel (Ref. 15) considered a wide range of corannulenes we shall examine principally those corannulenes made up of benzene rings and an inner ring size ranging from 5 to 18 carbons. Two other methods of nomenclature for these and related compounds have been proposed - coronaphenes and circulenes - but neither is as general as the one we propose (Refs. 16-18). Corannulenes may be considered a distinct type of annulenoannulenes, in which the two annulene components are concentric.

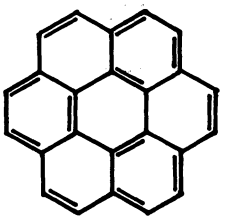


For those systems which contain an inner five-, six- or seven-membered ring it is likely that only those in which the inner annulene is all cis will exist as stable compounds:



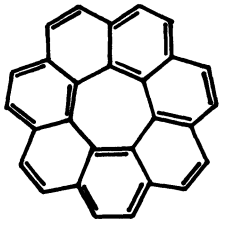
4

coranmulene[6^2,6^2,6^2,6^2,6^2]



5

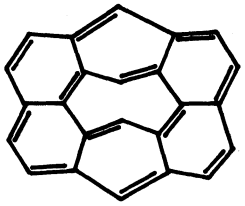
corannulene[6^2,6^2,6^2,6^2,6^2,6^2]



6

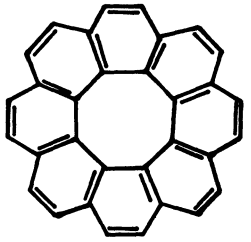
coranmulene[6^2,6^2,6^2,6^2,6^2,6^2,6^2]

However with an eight-membered ring the corannulene might have an inner pentalene-like ring or an all cis inner ring:



7

coranmulene[6^1,6^2,6^2,6^1,6^2,6^2]

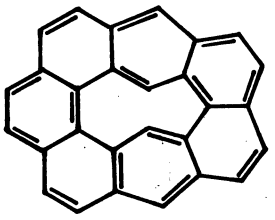


8

corannulene[6^2,6^2,6^2,6^2,6^2,6^2,6^2,6^2]

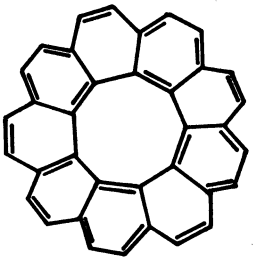
Of course in 7 there would be severe steric crowding of the inner two hydrogens. Note that 7 has a 16 carbon periphery and 8 twenty-four carbons.

Corannulenes with an inner ring of nine carbons could have their inner ring as an indene or as an all cis 9-membered ring:



9

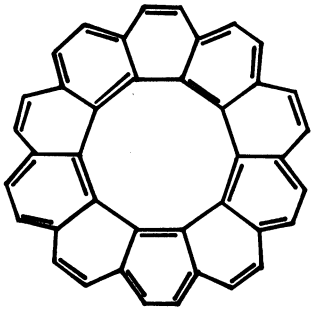
corannulene[$6^1,6^2,6^2,6^1,6^2,6^2,6^2$]



10

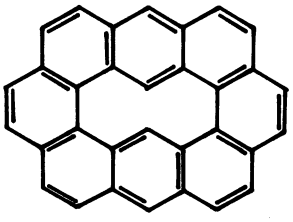
corannulene[$6^2,6^2,6^2,6^2,6^2,6^2,6^2,6^2,6^2,6^2$]

In the case of an inner ten-memebered ring we have considered corannulenes with an inner ring like the periphery of an all <u>cis</u> [10]annulene, naphthalene, azulene or bicyclo[6.2.0]decapentaene:



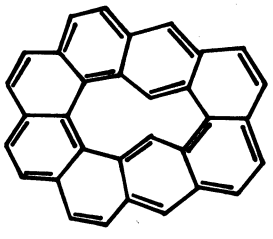
11

corannulene[$6^2,6^2,6^2,6^2,6^2,6^2,6^2,6^2,6^2,6^2,6^2$]



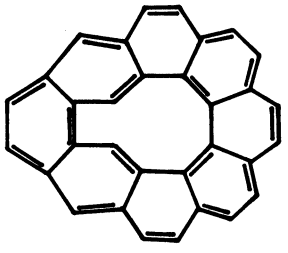
12

corannulene[$6^1,6^2,6^2,6^2,6^1,6^2,6^2,6^2$]



13

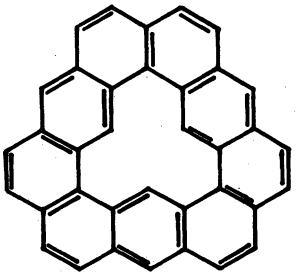
corannulene[$6^1,6^2,6^2,6^2,6^2,6^1,6^2,6^2$]



14

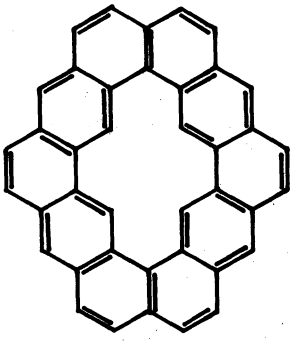
corannulene[$6^2,6^2,6^2,6^2,6^2,6^1,6^2,6^1$]

We have also selected a number of larger systems:



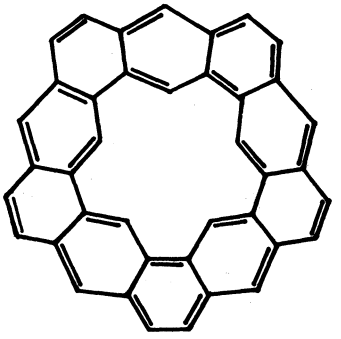
15

corannulene[$6^2,6^1,6^2,6^2,6^1,6^2,6^2,6^1,6^2$]



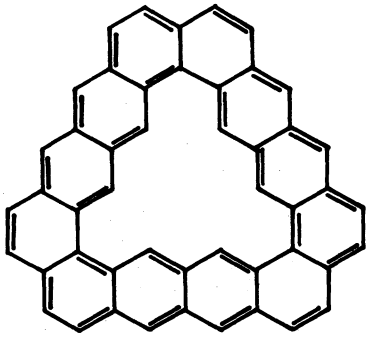
16

corannulene[$6^2,6^1,6^2,6^1,6^2,6^2,6^1,6^2,6^1,6^2$]



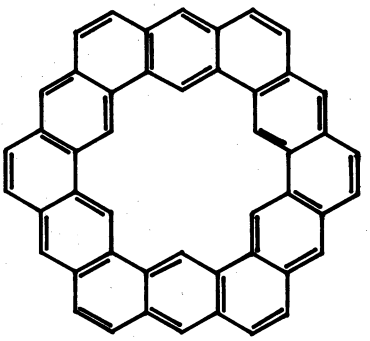
17

corannulene[$6^2,6^1,6^2,6^1,6^2,6^1,6^2,6^1,6^2,6^1$]



18

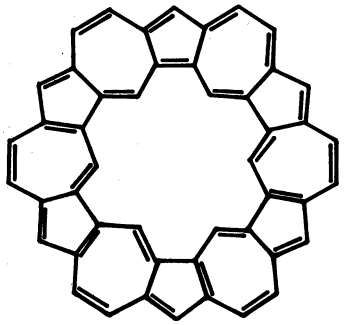
corannulene[$6^2,6^1,6^1,6^2,6^2,6^1,6^1,6^2,6^2,6^1,6^1,6^2$]



19

corannulene[$6^1,6^2,6^1,6^2,6^1,6^2,6^1,6^2,6^1,6^2,6^1,6^2$]

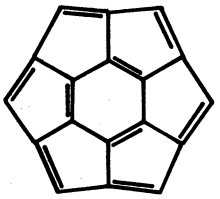
We have also considered two systems which are not made up of six-membered rings. Compound 20 is built of azulene units (Ref. 19).



20

corannulene[$5^1,7^2,5^1,7^2,5^1,7^2,5^1,7^2,5^1,7^2,5^1,7^2$]

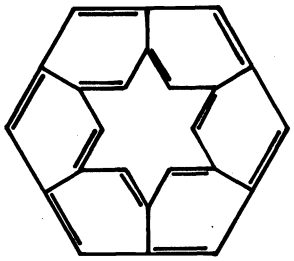
Compound 21 is built of five-membered rings around a central ring of six and may be contrasted with 4 which is made of six-membered rings around a central cycle of five.



21

corannulene[$5^1,5^1,5^1,5^1,5^1,5^1$]

Finally, we have looked at



22

coranmulene[6^1,6^1,6^1,6^1,6^1,6^1]

The results of our calculations are summarized in Table 2. Examination of these numbers leads to no simple conclusion. There is not a correlation between the number of electrons or carbon atoms in the inner and outer rings and REPE. Compounds 4-19 are all of roughly equal aromaticity. Even those systems (7, 8 and 15) with Hückel 4n inner and outer rings are not of significantly different REPE from those with Hückel 4n + 2 inner and outer rings. Kekulene (19) and corannulene (4) are the only ones of these systems which have so far been synthesized (Refs. 13 & 14) and their benzenoid behavior is in support of our results.

Table 2. Resonance energies per π electron of selected corannulenes

compound	inner ring size	outer ring size	REPE (β)
4	5	15	+0.049
5	6	18	+0.049
6	7	21	+0.049
7	8	16	+0.042
8	8	24	+0.048
9	9	19	+0.043
10	9	27	+0.049
11	10	30	+0.049
12	10	22	+0.047
13	10	22	+0.047
14	10	22	+0.047
15	12	24	+0.045
16	14	26	+0.045
17	15	25	+0.045
18	18	30	+0.040
19	18	30	+0.045
20	18	30	+0.021
21	6	12	+0.001
22	12	12	+0.019

The results for compounds 4-19 are all as one would expect qualitatively from Randić's (Refs. 4 & 5) method of conjugated circuits, i. e., the number of 6-membered circuits far outweighs the number of peripheral circuits. For example, kekulene has 200 resonance

structures. Four of these 200 contain only the 18- and 30-membered peripheral circuits. All others contain 6-membered circuits, and kekulene is in fact benzenoid. The same results are obtained by the method of Herndon through enumeration of Kekulé structures (Ref. 20).

Compounds 20 and 21 can be explained in a similar way. 20 contains azulene circuits and its REPE of 0.021 is computed to be quite close to that of azulene (REPE = 0.023). 21 does not contain pentalene circuits, but only the inner benzene circuit (aromatic) and and the outer circuit of 12 (antiaromatic). In agreement with this, it is predicted to be nonaromatic; not like the antiaromatic pentalene.

Compound 22 provides a surprise. It has only four resonance structures; each has only the inner circuit of 12 electrons and the outer circuit of 12 electrons. These are 4n circuits. There are no six-membered benzene circuits. In spite of this, we compute an REPE of +0.019 which would (neglecting strain and steric crowding of the central hydrogens) make 20 nearly as aromatic as azulene. Finally, corannulenes serve as a testing ground for the interplay of aromaticity vs. strain. Obviously, the REPE method does not take this latter aspect into account.

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