Conjugation and Aromaticity of Corannulenes[†]

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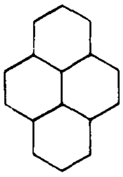
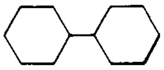
Abstract: A number of corannulenes are examined from a graph theoretical point of view and classified according to their content of $4n + 2$ and/or $4n$ conjugated circuits. Expressions for the resonance energy are given, and resonance energies were calculated. The work illustrates how seemingly similar skeletal forms of fused polycyclic rings can have profound structural differences and vary in their aromatic character from fully aromatic to totally antiaromatic systems. Significance of small rings points to limitations of the perimeter model, and occurrence of a significant number of some larger conjugated circuits points to the need for inclusion of higher terms, terms customarily neglected in approximate resonance-structure calculations.

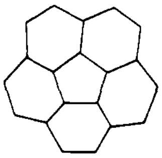
The Hückel $4n + 2$ rule has been hailed as one of the most significant contributions of recent theoretical chemistry that has immediate meaning to the experimental chemist.[1] It proved its validity in application to annulenes even though it is assumed to apply to a much wider assembly of conjugated polycyclic systems.[2-4] Extension of the simple argument to polycyclics lacks theoretical justification. The validity of the $4n + 2$ rule is not due to particular virtues of an approximate molecular orbital method but due to inherent reflection of molecular topological features within the simple Bloch assumption on the nearest-neighbor approximation,[5] implemented by Hückel in his historical work on benzene.[6] Difficulties in proving the Hückel $4n + 2$ rule are well-known, and MO formalism as such is not suited for justifying the topological rule of substantial stability of $4n + 2$ π-electron systems. Already pyrene and even diphenyl require some *additional* clarifications, such as help of perturbation model.[2,7] The situation becomes more complex for nonbenzenoid systems and nonalternants in particular, not to mention additional complications in the case of ions and radicals. Corannulenes appear to be a relatively well defined family of compounds, rich in structural variations, hence suited for testing theoretical models. Corannulenes are defined as compounds possessing an inner annulene system to which are fused peripheral rings in such a way that all valencies of the core ring are used. In recent years there was considerable interest in the preparation of corannulenes and their physical and chemical properties.[8-16] In addition, a lot of theoretical research is devoted to this class of polycyclic conjugated systems.[14,17-23] There were several other names proposed for corannulenes. The name *circulene* was proposed by Dopper and Wynberg,[12] because of the circular arrangement of aromatic rings in the molecule. Other researchers have used names like *corona-condensed systems*[20] and *coronaphenes*.[16] However, corannulene is the oldest,[8,18] and most often used,[22] name for the rings of rings.


pyrene


biphenyl

Regular corannulenes may be denoted as $[m,l,k]$ systems, where m is the number of condensed rings, l is the number of carbon atoms in a ring, and k is the number of bonds in one ring that appear in the inner polygon of corannulene. Agranat at al.[22] proposed a more general nomenclature for corannulenes than the above. After the word corannulene they put a set of superscripted numbers in square brackets. These numbers specify the size of constituent rings which are linked to make the corannulene. The superscript gives the number of carbon atoms in the specified constituent ring, lying in the outer periphery of the molecule and unshared by adjacent rings. For example, coronene, which can be viewed as a member of the corannulene family, will be denoted by these systems of nomenclature as either [6.6.1]corannulene or corannulene $[6^2.6^2.6^2.6^2.6^2.6^2]$.

[5.6.1]Corannulene or corannulene $[6^2.6^2.6^2.6^2.6^2]$, the first nonbenzenoid member of the family to be synthesized in 1966 by Barth and Lawton,[8] presented interesting theoretical questions concerning its structure, such as the degree of nonplanarity and strain, the possible role of ionic valence structures, etc. The



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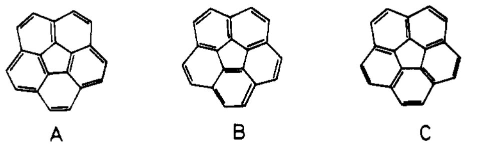
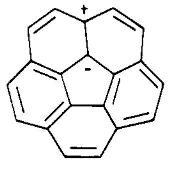
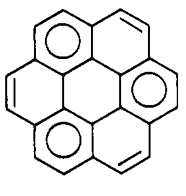


Figure 1. Three distinctive (symmetry unrelated) Kekulé valence structures of corannulene.

molecule also raises some problems with existing schemes on characterization of its aromatic character. It is a 20-π-electron system, and in contrast to pyrene it is not apparent here how perturbation approach is to be applied unless one invokes ionic structures. Formally one can represent the central ring as a cyclopentadienyl ring and the outer ring as a 14-π-electron (positvely charged) subsystem and then use the language of the perturbation method. However, this approach tends to give



prominence to the central ring of corannulene, yet if we make a comparison with coronene and follow the arguments of Clar,[23] then the central ring should be viewed as devoid of aromatic content!



All these difficulties are simply and elegantly resolved if one uses the concept of conjugated circuits[24] as the basic structural component. We mentioned the difficulties of the perimeter model because the model appears to be still used among chemists[25] while it ought to be abandoned. It not only cannot give an answer in a number of cases, like corannulene discussed here, but it can give incorrect answers, and it misleads one into believing that a large molecular periphery plays a critical role for determining aromatic and other molecular properties while the crucial role is played by smaller rings which can sustain conjugated circuits distribution. In an effort to draw proper attention to the graph theoretical approach to chemical structure in general and to conjugation and aromaticity in particular, we undertook the task to examine more closely a number of corannulenes and predict their characteristics.

Conjugated Circuits in Corannulenes

Conjugated circuits have been defined as those circuits *within* individual Kekulé valence structure in which there is a regular alternation of the formal CC single and double bonds. In Figure 1 we show three symmetry-unrelated Kekulé valence forms of corannulene. Conjugated circuits of the first structure are all depicted in Figure 2.

Graph theoretical viewing of corannulene consists in examination of individual Kekulé valence structures and enumeration of their conjugated circuits. Each structure is thus replaced by its content of conjugated circuits. Besides counting conjugated circuits it is advantageous to count also all disjoint conjugated circuits, i.e., those combinations of the conjugated circuits already found which have no common CC bonds. As has been discussed elsewhere[26] the total of all conjugated circuits *within* a single Kekulé valence structure (i.e., including into the count also disjoint conjugated circuits) is exactly $K-1$, where K is the number of Kekulé valence structures. Hence, for corannulene $K-1=10$, each Kekulé structure contributing ten terms, as shown below:

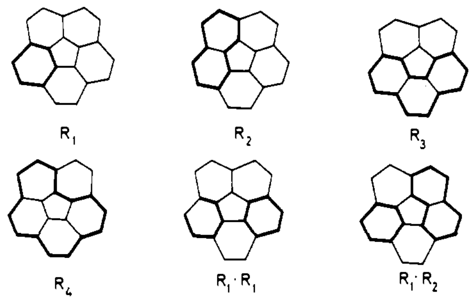


Figure 2. Conjugated circuits of the Kekulé structure A in Figure 1. (Only six out of ten possibilities are shown. The other four are related by symmetry.)

structure A:

$$2R_1 + 2R_2 + R_3 + 2R_4 + (R_1R_1) + 2(R_1R_2)$$

structure B:

$$3R_1 + 2R_2 + R_3 + 2(R_1R_1) + 2(R_1R_2)$$

structure C:

$$5R_1 + 5(R_1R_1)$$

We use the symbol R_1 for conjugated rings of benzene, R_2 for conjugated rings involving 10 carbon atoms, R_3 for conjugated circuits involving 14 carbon atoms, and finally R_4 for conjugated rings involving 18 carbon atoms. In general, R_n stands for a conjugated circuit (ring) of size $4n+2$. The "product" (R_1R_1) signifies two disjoint (i.e., independent and not having common CC bonds) conjugated rings having six carbon atoms, and similarly (R_1R_2) represents disjoint conjugated circuits within a single Kekulé valence structure having six and ten carbon atoms. Later we will have conjugated circuits involving $4n$ carbon atoms, and these will be symbolized with the letter Q_n, while (R_iQ_j) and (Q_iQ_j) will represent *disjoint* conjugated circuits of $4n+2$ with $4n'$ and $4n$ with $4n'$ type, respectively.

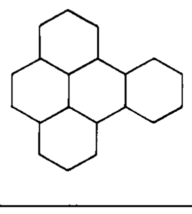
The expression for molecular resonance energy (RE) is obtained by adding the results for individual Kekulé valence structures and dividing the result by K:

RE:

$$(30R_1 + 20R_2 + 10R_3 + 10R_4 + 20(R_1R_1) + 20(R_1R_2))/11$$

Observe that in this particular example we have only conjugated circuits of size $4n+2$.

As has been described in the discussion of aromaticity and conjugation in benzenoid and other conjugated polycyclic hydrocarbons,[24,27] we consider a system *aromatic* (by definition!) if it contains only $4n+2$ conjugated circuits. Hence, corannulene is seen to be an aromatic compound and should display properties typical of other undisputed aromatic structures. If we adopt for the parameters R_n the following values (based on work of Dewar and de Llano,[28] who made SCF π-MO RE calculations on numerous polycyclic hydrocarbons, making thus possible to determine the values for R_n),[24] $R_1 = 0.869$ eV $R_2 = 0.246$ eV, $R_3 = 0.100$ eV, and $R_4 = 0.041$ eV, we obtain for RE of corannulene 2.945 eV. This value is comparable to RE of benzo[*d*]pyrene, also a $C_{20}H_{10}$ hydrocarbon: another polycyclic benzenoid system with $K = 11$ (RE = 2.930 eV). Not only is RE of a similar magnitude



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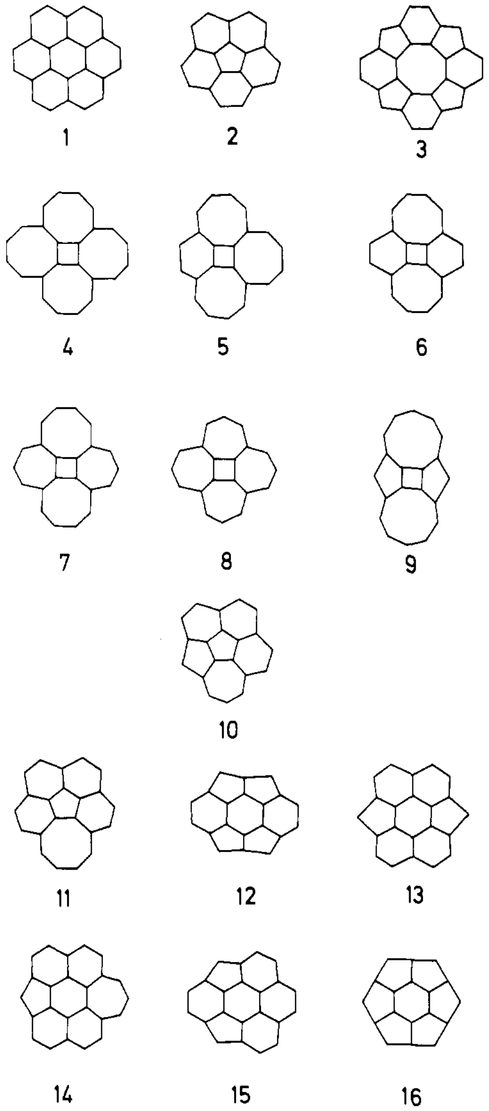

Figure 3. Corannulenes examined in this work.

for the two isomeric $C_{20}H_{10}$ hydrocarbons, but more importantly, both molecules have only $4n + 2$ conjugated circuits and thus belong to the same class as far as their conjugation type indicates. Appearance of only $4n + 2$ conjugated circuits is reminiscent of the Hückel $4n + 2$ rule that is supposed to indicate systems of special stability. If we view the molecule as a superposition of conjugated circuits, rather than superposition of Kekulé valence structures, we immediately see that to each component the Hückel rule individually applies; hence, it is a valid conclusion that corannulenes *are* Hückel $4n + 2$ type, even if the Hückel model could not be applied to give this conclusion. In fact, it would be more correct to refer to $(4n + 2)$ conjugation and $4n$ conjugation, thus avoiding reference to a model that is today only of historical and educational distinction.

Other Corannulenes

In Figure 3 we show corannulenes studied in this work. Except for the first three compounds we followed the arrangement based on the size of the central ring, discussed already in the literature,[18] where a classification based on ring types was proposed supplemented with description of the arrangement of rings. We have excluded in the present study ions, but they are also subject to the present type analysis as demonstrated on ions (cations, anions, and dications) of numerous conjugated polycyclic systems.[29,30]

Table I. Expressions for Molecular Resonance Energies of Corannulenes of Figure 2

no.	K	expression for the resonance energy
2	11	$(30R_1 + 20R_2 + 10R_3 + 10R_4 + 20(R_1R_1) + 20(R_1R_2))/11$
3	14	$(16R_1 + 16R_3 + 32R_4 + 8R_6 + 4Q_2 + 24Q_3 + 20Q_4 + 42Q_5 + 4Q_6 + 8(R_1R_1) + 4(Q_2Q_5) + 8(Q_3Q_3))/14$
4	9	$(8R_2 + 9R_3 + 8R_4 + 4Q_1 + 16Q_2 + 3Q_4 + 12Q_5)/9$
5	9	$(4R_1 + 6R_2 + 6R_3 + 14R_4 + 4Q_1 + 14Q_2 + 4Q_3 + 6Q_4 + 2Q_5 + 4(R_1Q_2) + 4(R_4Q_1) + 4(Q_2Q_2))/9$
6	9	$(8R_1 + 4R_2 + 4R_3 + 4Q_1 + 12Q_2 + 10Q_3 + 15Q_4 + 4(R_1R_1) + 4(Q_2Q_2) + 4(Q_1Q_4))/9$
7	6	$(4R_2 + 2R_3 + 8R_4 + 4Q_1 + 4Q_2 + 4Q_4)/6$
8	4	$(4Q_1 + 4Q_4 + 4(Q_1Q_4))/4$
9	4	$(4Q_1 + 4Q_4 + 4(Q_1Q_4))/4$
10	7	$(8R_1 + 10R_2 + 8R_3 + 6R_4 + 2Q_2 + 4Q_3 + 4(R_1R_2))/7$
11	11	$(24R_1 + 12R_2 + 4R_3 + 2R_4 + 6Q_2 + 8Q_3 + 6Q_4 + 8Q_5 + 12(R_1R_1) + 8(R_1R_2) + 8(R_1Q_2) + 8(R_1Q_3) + 4(R_2Q_2))/11$
12	8	$(8R_1 + 4R_2 + 8R_3 + 4R_4 + 8Q_2 + 32Q_3 + 2(R_1R_3) + 2(R_1Q_3) + 4(Q_2Q_2))/8$
13	8	$(12R_1 + 8R_2 + 4R_3 + 2Q_4 + 8Q_6 + 4(R_1Q_4))/8$
14	8	$(12R_1 + 8R_2 + 4R_3 + 20R_4 + 8R_5 + 4(R_1R_4))/8$
15	10	$(18R_1 + 12R_2 + 8R_3 + R_4 + 9Q_3 + 26Q_4 + 7Q_5 + 3(R_1R_1) + 4(R_1Q_3) + 4(R_1Q_4))/10$
16	4	$(4R_1 + 4Q_3 + 4(R_1Q_3))/4$

Table II. Numerical Values for the Resonance Energies Derived from the Expressions in Table I Using the Parameters Given in the Text and Neglecting "Product" Contributions as well as Conjugated Circuits Having More Than 18 Carbon Atoms[a]

no.	K	Re($4n + 2$), eV	Re($4n$), eV	Re, eV	A or AA,[b] %
2	11	2.945		2.945	100.0 A
3	14	1.201	−0.471	0.730	43.6 A
4	9	0.355	−1.561	−1.206	62.9 AA
5	9	0.681	−1.518	−0.837	38.1 AA
6	9	0.944	−1.178	−0.233	11.0 AA
7	6	0.252	−1.467	−1.215	81.4 AA
8	4		−1.660	−1.660	100.0 AA
9	4		−1.660	−1.660	100.0 AA
10	7	1.494	−0.214	1.280	74.9 A
11	11	2.208	−0.387	1.821	70.2 A
12	8	1.113	−1.050	0.063	2.9 A
13	8	1.600	−0.150	1.450	87.9 A
14	8	1.720		1.702	100.0 A
15	10	1.944	−0.291	1.653	74.0 A
16	4	0.869	−0.150	0.717	70.4 A

[a] Re($4n + 2$) and Re($4n$) represent the partition of RE into positive and negative contributions. [b] A = aromatic; AA = antiaromatic.

Tables I and Table II summarize the results of the analysis. In Table I we give the expressions for molecular RE in terms of various R_n and Q_n conjugated circuits, and in Table II we give the numerical values based on the formulas of Table I and the numerical values already indicated for R_n and the following values for Q_n: $Q_1 = -1.60$ eV, $Q_2 = -0.45$ eV, $Q_3 = -0.15$ eV, and $Q_4 = -0.06$ eV. All the corannulenes considered are relatively small structures, and by a careful inspection of the individual Kekulé valence formulas one can discern all conjugated circuits involved. In Figure 4 we show few Kekulé formulas for selected corannulenes and their decomposition in order to indicate the degree of work involved and would like to encourage the reader to verify and locate all the conjugated circuits. Even though the molecules are relatively simple and have not many rings, it is sometimes tedious, even frustrating, to locate one or two last missing circuits. A computer program is, however, available for recording all conjugated circuits (and plotting all Kekulé valence structures)[31] which may be desirable when considering even large polycyclic structures. However, there is a relatively simple, direct, and systematic way of finding all conjugated circuits.[32] We will illustrate it on the

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[31] Stolow, R.; Harris, F. E.; Randić, M. to be published. The program is installed at the Chemistry Department, Tufts University, Medford, MA 02155 (correspondence to Professor Stolow at above address).

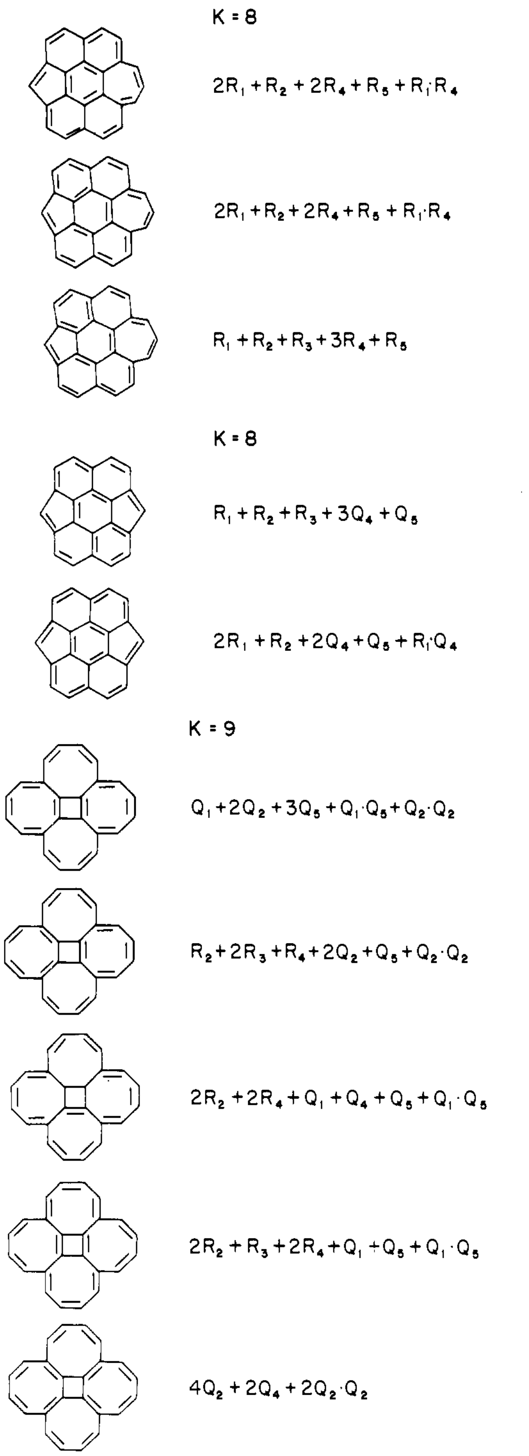

Figure 4. Some Kekulé valence structures for selected corannulenes of Figure 3 and the associated decomposition of the conjugation into conjugated circuits. The number of contributing terms is determined by *K* - 1.

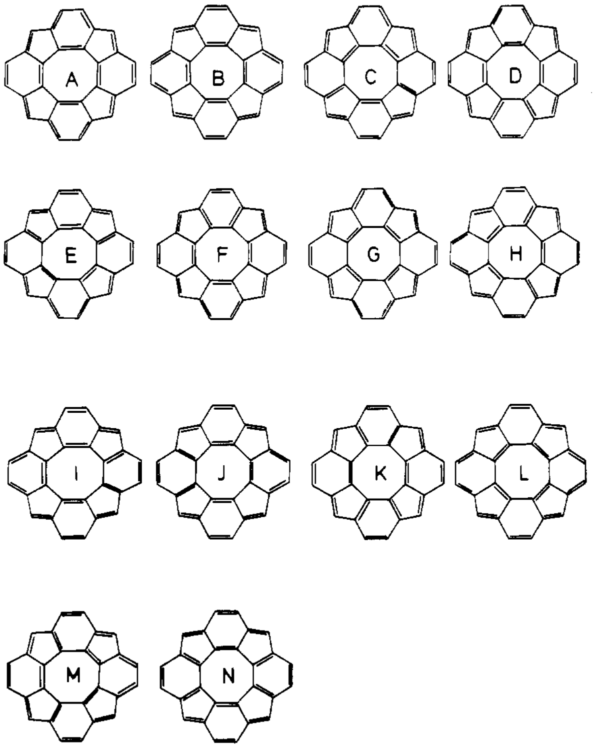

Figure 5. Corannulene **3**: all Kekulé valence structures arbitrarily labeled.

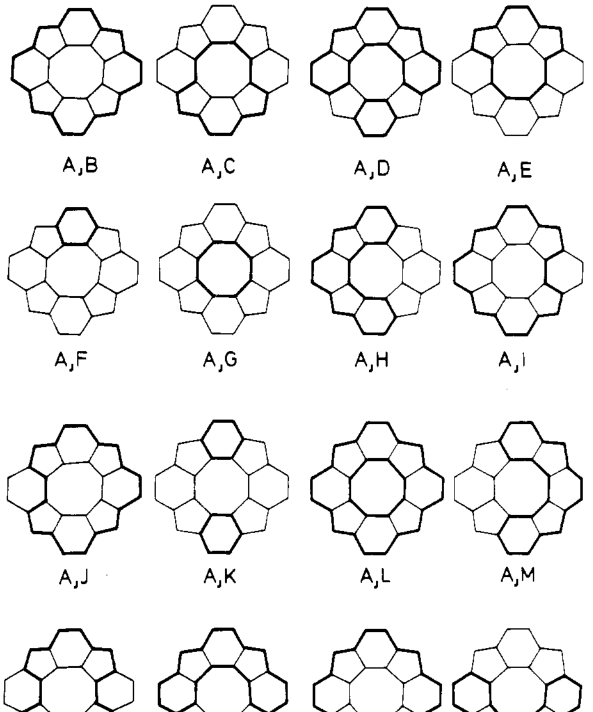

Figure 6. Conjugated circuits derived by pairwise superposition of valence structures. All possibilities involving structure A and few for structure B are shown.

case of tetramethenotetraphenylene (**3**). The following is the procedure: construct all Kekulé valence structures[31,33,34] and label them arbitrarily, as we have with letters A–N (Figure 5). It is very convenient if these valence structures are drawn on transparencies. Consider now pairwise superpositions: (A,B), (A,C), (A,D), ..., (M,N). If transparencies are unavailable, one can simply place one structure over the other, say A over B. The result will give a conjugated circuit(s), which will appear as a solid circuit(s), as illustrated in Figure 6 for a few initial combinations. After completing the process for all pairs one obtains all conjugated circuits. All pairs mean here (A,B) and (B,A), which of course give the same result. In the case of corannulene **3** we have $^1/_2$ (14·13), in all 91 pairs, but the work can be further simplified when there is some symmetry (as in this case) by not considering

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Table III. Predicted Resonance Energies for Corannulenes Suspected To Have Positive Aromatic Dominant Component

no.	K	conjugated circuits count	Re($4n + 2$), eV	Re($4n$), eV	RE, eV	A or AA, %
17	4	$4R_1 + 4R_4 + 4(R_1R_4)$	0.91		0.91	100.0
18	10	$16R_1 + 14R_2 + 8R_3 + 8R_4 + 8Q_4 + 26Q_5 + 4Q_6 + 4(R_1R_1) + 4(R_1Q_4) + 6(R_1Q_5)$	1.815	−0.48	1.34	58.2
19	12	$24R_1 + 16R_2 + 12R_3 + 6Q_3 + 12Q_4 + 22Q_5 + 8Q_6 + 8(R_1R_1) + 10(R_1Q_3) + 8(R_1Q_4) + 4(R_1Q_5) + 2(R_2Q_3)$	2.166	−0.24	1.93	90.0
20	10	$18R_1 + 12R_2 + 16R_3 + 24R_4 + 8R_5 + 2(R_1R_1) + 2(R_1R_2) + 4(R_1R_3) + 4(R_1R_4)$	2.118		2.12	100.0
21	12	$24R_1 + 22R_2 + 24R_3 + 22R_4 + 8R_5 + 8(R_1R_1) + 8(R_1R_2) + 8(R_1R_3) + 4(R_1R_4) + 4(R_2R_2)$	2.464		2.46	100.0
22	7	$10R_1 + 4R_2 + 10R_4 + 2R_5 + 8Q_3 + 4Q_4 + 2(R_1R_4) + 2(R_2R_2)$	1.524	−0.206	1.32	88.0
23	7	$8R_1 + 4R_2 + 12R_3 + 8R_4 + 4R_5 + 4(R_1R_4) + 2(R_2R_2)$	1.352		1.35	100.0
24	7	$8R_1 + 6R_2 + 10R_3 + 10R_4 + 4R_5 + 4(R_1R_4)$	1.404		1.40	100.0
25	7	$8R_1 + 6R_2 + 10R_3 + 10R_4 + 4R_5 + 4(R_1R_4)$	1.404		1.40	100.0
26	5	$6R_1 + 2R_2 + 6R_4 + 2R_5 + 4(R_1R_4)$	1.190		1.19	100.0
27	5	$6R_1 + 2R_2 + 6R_4 + 2R_5 + 4(R_1R_4)$	1.190		1.19	100.0

pairs that are symmetry equivalent to those already examined. For example, A and B are symmetry related (rotated by 90°); hence (B,X) should give the same result as (A,C) and (B,Y) as (A,D) and so on. That indeed this is correct can be seen from Figure 6, where besides all combinations involving Kekulé valence structure A we included a few with the valence structure B. The conjugated circuits involving structure B do not come in the same order. If we rotate valence structure C by 90° (clockwise) we obtain structure M; hence (B,C) becomes equivalent to (A,M) (which has to be rotated counterclockwise for full overlapping of the two diagrams).

Discussion

From Table II we immediately see how heterogeneous is the group of corannulenes considered. If we look at the computed RE's we have values as high as 1.821, 1.702, 1.653, and 1.450 eV for corannulenes 11, 14, 15, and 13, respectively, and values as low as −1.660, −1.215, −1.206, and −0.837 eV for corannulenes 8 and 9, 7, 4, and 5, respectively. The former group has relatively large RE and should display predominant aromatic characteristics. The index A (aromaticity index) generally parallels RE values, but it more precisely describes the percentage of the mixture of $4n + 2$ and $4n$ contributions to RE. Besides corannulene **2** the only other 100% aromatic corannulenes are **14** and **17** of Figure 7 and Table III. The latter structure represents a 6-annulene core and 18-annulene periphery, just as in coronene, except that the two annulene cocentric components cannot be connected with CC double bonds and thus have disjoint conjugate systems analogous to perylene, which is built from two disjoint π-electron naphthalene moieties. Such systems were termed "conjugation deficient", and the relatively small K value illustrates some "ridigity" of the π-system in such systems. Recently,[35] a parameter D, "innate degree of freedom of π-electron couplings", was suggested as a measure of long-range localization and delocalization of π-electron couplings which even more vividly indicates deficiency of aromatic content in structures with fixed bond types. For **16** we have $D = 8$, which can be compared with $D = 55$ for coronene.

Among the corannulenes of Table II structures **8** and **9** are fully antiaromatic, and very high antiaromatic behavior is to be excepted from **7** and **4**, and then **5** and **6**. As one sees from Figure 3 all these compounds have a central four-membered ring and, therefore, contributions Q_1 which make a large negative donation to RE. In **10** the negative contributions come from the pentalene part, while in **11** the antiaromatic contributions are due to the eight-membered ring. Both the pentalene and cyclooctatetraene fragments contribute Q_2 (or higher negative terms when combined with other rings); hence **10** and **11** have visibly higher aromatic content, because Q_2 does not make such a dominant contribution as Q_1. Finally, **12** is an interesting corannulene, for which Platt predicted extra stability in view of its 14 π-electron perimeter. With due respect for the pioneering work of Platt on aromaticity and conjugation,[36] subtleties of π-electron couplings could not be resolved simply from the *count of π-electrons* but rather, as we advocate here and elsewhere, from the *count of qualified substructure*: conjugated circuits. In **12** two pentalene fragments, each contributing Q_2, accumulate sufficient amount of negative contributions that almost completely cancel out positive contributions arising from $4n + 2$ conjugated circuits, and the molecule is predicted as essentially nonaromatic, i.e., with an index of aromatic character of almost zero.

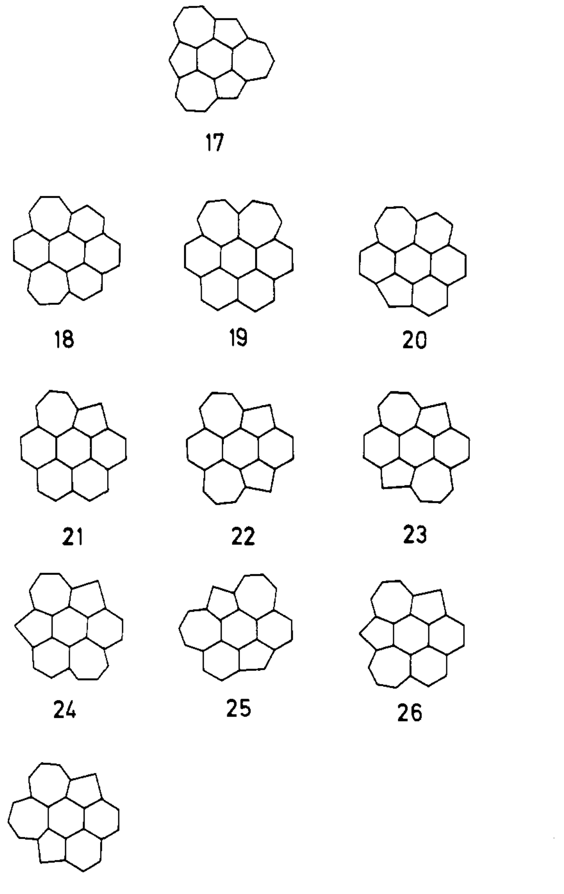

Figure 7. Additional corannulene investigated. Structures **18**–**27** are expected to show positive dominant contributions to RE and relatively high aromatic character, as in their construction one avoided proximity of small rings contributing to Q_1 and Q_2.

Further Predictions

The results of Table II, combined with the information of Table I, can indicate structural groupings that will either increase the resonance stabilization (i.e., increase RE) or decrease the resonance stability. A five-membered ring alone or combined with seven-membered ring (as in azulene, or structure **14**) leaves the system of $4n + 2$ type. If we have five-membered rings, preferably, they

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[35] Randič, M., to be published.

[36] Platt, J. R. In "Encyclopedia of Physics"; Flügge, S., Ed.; Springer: Berlin, 1961; Vol. 37, p 173.

should be separated by even-membered rings (such as in **13**) as this will increase the subscript n in Q_n and lead to smaller negative contributions. In Figure 7 we have constructed few additional corannulenes trying to produce structures with relatively modest positive RE. Table III shows how well we accomplished this goal. The exercise is meant to indicate how one can use the particular approach and *anticipate* the character of compounds in advance. This is not only of interest as a way of exposing the model for scrutiny of experimental verification, an ultimate judge, but the approach may well *suggest* to experienced chemists desirable routes for synthesis, if one is willing to trust the model before attempting to dispute it. There is, of course, ample evidence in supporting the model based on conjugated circuits; the question is perhaps to see, with accumulation of experience, whether currently adopted numerical parameters may have restricted application or if perhaps additional components may make important contribution. In the case of corannulenes we have seen that some large conjugated circuits, which normally make small contributions, can appear in the count with a large coefficient. Thus, in the case of **12** there are 32 Q_3 terms, and even when $Q_3 = -0.15$ eV, the total of 32 such terms makes a visible contribution: -0.533 eV. This, of course, is not negligible at all. In the case of corannulene **13**, the contribution from higher $4n$ conjugated circuits is small (structure is found to be 87.9% aromatic), but if these were completely neglected, as is done within the structure-resonance model of Herndon,[37] one would not make an important error in RE, but the compound would be incorrectly classified, as 100% aromatic. The same again is the case with **15**. Finally, we would like to point out some similarities in the counts of conjugated circuits in *different* structures. The situation is well illustrated by **13** and **14** which differ in size of a single odd-membered ring which is at the periphery. Comparison of the corresponding rows in Table I for the expression of RE shows term by term the same coefficients in the counts of all conjugated rings, except a few involving the seven-membered ring. The seven-membered ring represents an increase of two carbon atoms over the five-membered ring, which means that the conjugated circuits involving the five-membered ring in **13** that give rise to Q_4 and Q_5 will now generate R_4 and R_5. The situation is similar to that found in ions of polycyclic conjugated hydrocarbons with addition or subtraction of an electron changes a $4n$ circuit conjugated into a $4n + 2$ circuit and vice versa.[29] In a somewhat different connotation the similar dependence of the *character* of the system on cycle size has been found to hold also within the Hückel MO method.[38] By the same token we can from **14** obtain immediately the expression of corannulene in which both five-membered rings are replaced by seven-membered rings:

$$\mathrm{RE}\ (\mathbf{17}) = (12R_1 + 8R_2 + 4R_3 + 20Q_5 + 8Q_6 + 4(R_1Q_5))/8$$

The reason for the simplicity of such transformation is the fact that there are *only two odd-membered rings in the structure*, and since conjugated circuits are necessarily even circuits it follows that all such circuits have to involve *both* odd rings. Hence, the simple replacement of Q_n with R_n of Q_{n+1} (if both rings are increased) has limited application, nevertheless, when applicable, it offers the results immediately.

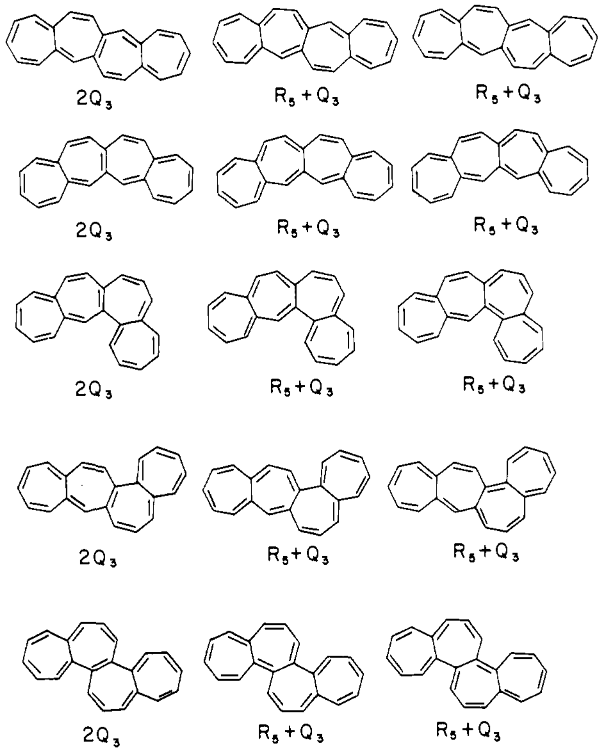

Figure 8. Kekulé valence structures for selected nonbenzenoid systems for which the graph theoretical approach predicts same stability while simple MO computations suggest somewhat different stability.

Comparison with Other Computations

This paper represents the first comprehensive study of resonance energies of corannulenes; in all we have examined 27 different structures. Occasionally a few corannulenes would appear in studies of a larger collection of structures, except for a paper by Agranat, Hess, and Schaad,[22] who considered 18 corannulenes, 16 of which consists only of fused six-membered rings around the central k-membered ring. The two sets of compounds, our 27 and 28 studied by Agranat et al., have only three compounds in common, one of which is coronene. Hence, there is little ground for making comparisons and discussing differences. In both studies [5.6.1]corannulene (compound **2** in this report) is found (excluding coronene, compound **1** in this report) to have the largest resonance energy. Here the two approaches agree. This, however, is not the case with structure **16**, for which we find appreciable resonance energy, while the approach of Agranat, Hess, and Schaad deprived the compound of any resonance energy. Hence, while at this moment we cannot decidedly give preference to one or the other scheme, it is important to recognize that they give different predictions! A close comparison of resonance energies for selected nonbenzenoid systems already points to *differences* between the Hückel-type MO computations, of which an illustration is the approach of Hess and Schaad,[39] who judiciously relate molecular stability to resonance energy per electron (REPE), of the scheme of Trinajstić and co-workers,[40] who use a hypothetical reference "system" derived by eliminating certain cyclic contributing terms, and the present graph theoretical scheme, which can be brought into mathematical equivalence to VB approach.[41] Besides different theoretical frame, observe that the graph theoretical scheme is flexible and can be parameterized to advanced SCF computations; hence, it should not be suprising that it gives in some instances different predictions than simple HMO computations would suggest. In particular we adopted the parameterization of R_n and Q_n to reproduce (or simulate) results of Dewar and de Llano for selected benzenoid and nonbenzenoid compounds. Alternative parameterizations have been hinted, e.g., by Schaad and Hess[42] in a recent comparison of various theoretical aromaticity indices and by Gomes[43] in a study of "general system of increments" and additivities in polycyclic hydrocarbons. While other authors may wish to stress similarities between different

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(37) Herndon, W. C. *J. Am. Chem. Soc.* **1973**, *94*, 2404. Herndon, W. C.; Ellzey, M. L., Jr. *Ibid.* **1974**, *96*, 6631. *Israel J. Chem.* **1980**, *20*, 270.

(38) Gutman, I.; Trinajstić, N. *Naturwissenschaften* **1974**, *60*, 475.

(39) Hess, B. A., Jr.; Schaad, L. J. *J. Am. Chem. Soc.* **1971**, *93*, 2413.

(40) Gutman, I.; Milun, M.; Trinajstić, N. *J. Am. Chem. Soc.* **1977**, *99*, 1692.

(41) As pointed out elsewhere (including ref 42 and 43 in particular) the two approaches are formally equivalent. They differ though on the conceptual side, one being graph theoretical, the other quantum mechanical. This only illustrates that the valence bond method has pronounced combinationial content, which has been reflected in early work of Pauling, Wheland, Rumer, and others.

(42) Schaad, L. J.; Hess, B. A. Jr. *Pure Appl. Chem.* **1982**, *54*, 1097.

(43) Gomes, J. A. N. F. *Theor. Chim. Acta* **1981**, *59*, 333.

approaches, we would like here to emphasize *differences*, because they will resolve the dilemma of which among currently available different schemes is most suitable for discussion of aromatic stabilities of polycyclic conjugated systems. Hence, we will make a comparison between two approaches: one based on conjugated circuits and the other on the Hückel MO REPE results of Hess and Schaad. We chose compounds taken from the work of Hess and Schaad.[44]

In Figure 8 we have illustrated five selected compounds and show their Kekulé valence structures. As one can verify by inspection all five compounds have the same decomposition of the conjugation: one structure with two Q_3 conjugated circuits and two structures with combination $R_5 + Q_3$. Hence, according to our graph theoretical viewing (and the same would follow from valence bond computations of Herndon's resonance theory[37]), all five compounds are equally stable (unstable). Yet REPE values separate these compounds into two groups: stable and unstable. The difference between the two groups admittedly is small: 0.004 and −0.006 are typical values for REPE for the two groups (in β units). We do not wish to blow out of proportion minor differences, but they clearly show that the two models are different and that the conclusions need not be comparable. Hückel MO is based on *adjacency* of π-electron carbon centers; VB model is based on *pairing* of such centers. The compounds for which one can anticipate different description are those in which not all adjacent π-electrons can be paired, e.g., perylene and *s*-indacene, the compounds with so-called "essentially single" CC bonds (Dewar was first to draw attention to such bonds).[2] Observe that compounds of Figure 8 have such essentially single CC bonds (cross CC bonds except for the central CC bond). Hence, we are not suprised that HMO gives a different account—which we believe is an artifact.

Concluding Remarks

Corannulenes provide a fine ground for testing various theoretical predictions concerning aromaticity and other aspects of chemistry of conjugated systems. Structures have relative simplicity, yet differ in a subtle way one from another. Critical here is the mode of fusion of rings and the clue to the properties that can be derived from the count of conjugated circuits associated with the collection of Kekulé valence structures. Among corannulenes considered here we have a case of 100% aromatic character to 100% antiaromatic, we have alternant systems as well as non-alternant, and we have systems that allow one to consider molecular perimeter as a component and those that do not allow such components, as corannulene itself, and thus throw considerable doubts on use of perimeter and perturbation method for prediction of molecular aromatic character. The original classification of corannulenes based on radial bonds and their (double bond) character can now be upgraded in extending the consideration to circuits, not only radical bonds. Some parallelism is apparent: systems in which all radial bonds are single became now systems with independent core and peripheral conjugated circuits. Although we have not introduced novel concepts here, application of the existing model of graph theoretical viewing of the collection of Kekulé valence structures can be unnecessarily tedious when applied to relatively complex situations. Hence, demonstration that the model works, is not difficult to implement, and gives useful deductions seems worthwhile. In fact, an important ingredient for application to large polycyclic systems is availability of the theorem which guarantees the number of components for each valence structure to be $K - 1$, and another ingredient, outlined here (and which has not yet been fully explored), is derivation of all conjugated circuits in a pairwise superposition of all Kekulé valence structures—which makes the search for the conjugated circuits straightforward even in unusually large systems. With the availability of computer programs for counting conjugated circuits and enumeration of Kekulé structures and their reproduction, we are in a position to extend the domain of theoretical consideration well beyond structures having few fused rings that typify current MO calculations (whether of an SCF type or even most simple models).

Registry No. 2, 5821-51-2; **3**, 28647-34-9; **4**, 72872-92-5; **5**, 90719-51-0; **6**, 64074-44-8; **7**, 90719-52-1; **8**, 90719-53-2; **9**, 90719-54-3; **10**, 90719-55-4; **11**, 90719-56-5; **12**, 518-65-0; **13**, 90719-57-6; **14**, 90719-58-7; **15**, 90719-59-8; **16**, 76297-29-5; **17**, 89168-42-3; **18**, 90719-60-1; **19**, 90719-61-2; **20**, 90719-62-3; **21**, 90719-63-4; **22**, 90719-64-5; **23**, 90719-65-6; **24**, 90719-66-7; **25**, 90719-67-8; **26**, 90719-68-9; **27**, 90719-69-0.

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(44) Hess, B. A.; Schaad, L. J. *J. Org. Chem.* **1971**, *22*, 3418.

(45) **Note Added in Proof**: Recently synthesis of the following corannulenes was reported: (a) (7)-circulene or [7,6,1]corannulene [Yamamoto, K.; Harada, T.; Nakazaki, M.; Naka, T.; Kai, Y.; Harada, S.; Kasai, N. *J. Am. Chem. Soc.* **1983**, *105*, 7171]. (b) Kekulene, [12,6,2]corannulene [Staab, H. A.; Diederich, F. *Chem. Ber.* **1983**, *116*, 3487].