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A CANONICAL ORDERING AND NOMENCLATURE FOR THE KEKULE STRUCTURES OF POLYBENZENES

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ABSTRACT: A systematic examination of the various Kekule structures that exist in polybenzenes suggests some important relationships that may be noted in the corresponding dual graph that is created by connecting adjacent double bonds. These relationships form the basis for an algorithm, based on examining the unifilar vs. spiro connections therein for cata-condensed ring systems and the unifilar vs. spiro vs. reticular connections for peri-condensed systems, to canonically order and name each of the possible Kekule structures of a given polybenzene. An additional observation applicable to many corona-condensed systems is also noted.

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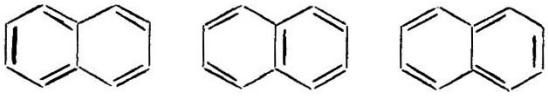
1. INTRODUCTION

This report systematizes and codifies the set containing all of the various main# Kekule structures that can be found in a given polybenzene (often referred to as a polyhex[1] or PAH6[2], etc.), using the synthetic nomenclature algorithm that we had developed earlier[3].

For any polybenzene, let us denote the number of rings by R, the number of Kekule structures by K, and a number which we shall call the "unifilar index" by U = 4R - 1. (The relationship of U to Taylor's classification scheme[4] of unifilar, reticular, spiro, etc. connections will be clarified shortly.) Meanwhile, note that for benzene R = 1, K = 2 and U = 3. For naphthalene (henceforth referred to as "dibenzene"[3]) R = 2, K = 3 and U = 7.

No consideration is given to any of the cross-bonded ("Dewar" benzene) forms.

At this point, let us examine each of the three Kekule structures for dibenzene (Figure 1). Observe that we may



a b c

FIGURE 1

standardize the drawing of the various Kekule structures by first positioning each of the compounds in accordance with Patterson's Rules [5]. Next starting from the leftmost edge (if more than one such edge exists, choose the uppermost) draw in a double bond, and all other unambiguous double bonds that this particular Kekule structure demands. In the case of Figure 1a, we have drawn in all five of the double bonds. For Figure 1b, on the other hand, the first double bond drawn is the one in the upper left hand corner. This necessitates drawing in a second double bond in the lower left hand corner. Now, however, there are two possible locations where the third double bond can be drawn (shown as b and c respectively). Because the bond in b is to the left of that in c we follow b first and draw in the mandated other two bonds to complete the resonance structure; then we similarly complete the resonance structure for c. That this technique produces a unique ordering is shown for the various tribenzenes in Figure 2.

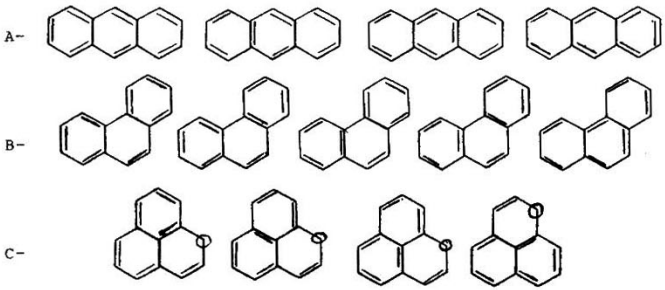


FIGURE 2

One further feature of this technique is the corroboration that C-Tribenzene is an impossible combination.#

Returning to the study of Figure 1, we may now create the respective dual graphs formed by drawing line segments between each pair of double bonds that are connected by a single bond (Figure 3)[6]. Note that in (a) and (c), the resultant dual

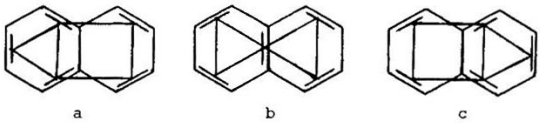


FIGURE 3

graph is a triangle (3-gon) unifilarly-joined to a rectangle (4-gon); while in (b), the dual is two spiro-joined 3-gons. For the first of these, the sum of the number of sides of the n-gons is the number that we designated as U above. Furthermore, we shall see that the sum of the n-gon sides for each spiro connection is one less than that in a unifilar connection. Let S denote the number of spiro connections.

2. CATA-CONDENSED POLYBENZENES

At this point, let us consider the sum of all combination of numbers of sides of a polygon that sum up to U - S for all possible values of S from 0 thru R - 1.

For R = 1, U = 3, and S = 0, thus we have the trivial case of one triangle as the dual of the Kekule structures.

For R = 2, U = 7 and S = 0 or 1; therefore, the possible unifilar connections are a triangle to a rectangle and a rectangle to a triangle (i.e., the mirror image) and the spiro connections is only that of two triangles. Furthermore, since a polygon must have at least 3 sides, this is the complete set of possibilities. These relations may be conveniently denoted by 3U4, 4U3 and 3S3. Also, all mirror images produce a

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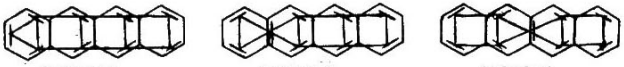
Note that the two pseudo-Kekule structures with the break in conjugation (free electron) in the middle, which are useful for certain types of studies, are not generated by this algorithm -- due to its left to right orientation.

3U4U4 3S3U4 4U3S3 4U4U3

A - Tribenzene

3U5U3 3U4S3 3S4U3 3S3S3 4U3U4

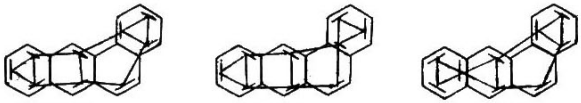
B - Tribenzene.



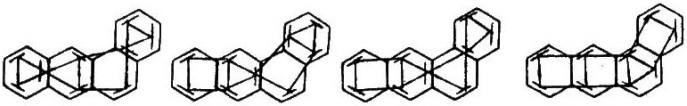
3U4U4U4 3S3U4U4 4U3S3U4

4U4U3S3 4U4U4U3

AA - Tetrabenzene



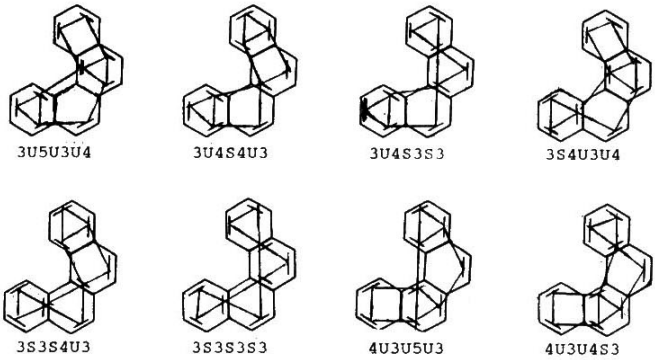
3U4U5U3 3U4U4S3 3S3U5U3



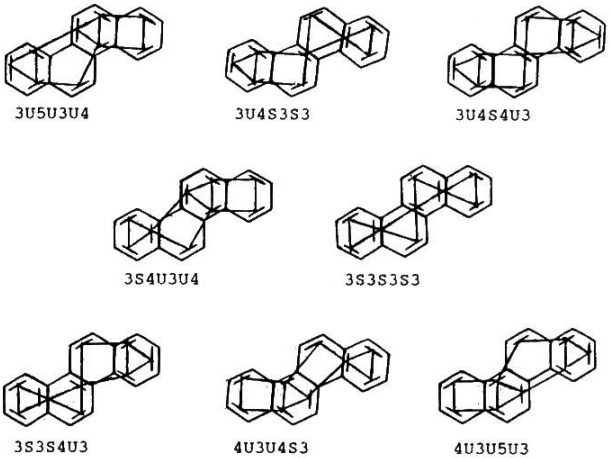
3S3U4S3 4U3S4U3 4U3S3S3 4U4U3U4

BA - Tetrabenzene

FIGURE 4 - Part 1



BB - Tetrabenzene



DB - Tetrabenzene

FIGURE 4 - Part 2

reverse code; i.e., 4U3 = 3U4. Figure 4 illustrates all of the viable cata-condensed[7] unifilar tri- and tetra-benzene resonance structures, along with their systematic development and a left-to-right sequential canonical name for each.

Next we observe that by tabulating all possible codes that sum to U - S, we have a means of generating all possible cata-condensed Kekule structures. Actually, for computer record-keeping purposes; we may simplify by listing U - 3R - S as an R-tuple sequence of digits. In Table 1, we have generated all the Kekule structures for dibenzene and the various tri- and tetra- benzenes and given a reason why only some of the numerical combinations actually correspond to a viable graph (and thus a potential polybenzene). Additionally we have correlated these configurations with the respective structures portrayed in Figures 3 and 4; e.g., BA4 means the fourth structure shown for BA-Tetrabenzene, etc.

Furthermore, at the top of Table 1 are listed the reasons why various numerical combinations are impossible. Justification is as follows:

An end ring can be attached to the residue of the molecule by either a double bond or a single bond. For a double bond, the dual contains the center point of the double bond as a vertex. This point is a spiro-connection to the residue. Consequently, the end ring will always generate a 3-gon as the dual of this part. For a single bond at the juncture, the dual has no edge coincident with the junction but has double bonds at the two contiguous edges of the residue. The connection of the midpoints of these double bonds creates an edge of the dual that is parallel to the single bond edge and thus creates a unifilar junction of polygons in the dual. Furthermore, we note that the number of double bonds emanating from a single benzene ring are either 0, 2, 4 or 6 (Figure 5)[#]. This gives rise to the corresponding part of the dual graph being a 3-gon, 4-gon, 5-gon and 6-gon respectively. When the benzene ring being

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Similarity to this set of drawings was obtained by Cyvin[8] in the study of a different set of properties of polybenzenes.

TABLE 1

UNIFILAR CATA-CONDENSED RING SYSTEMS

OBSERVATIONS

1. A chain can end in S3, U3, or U4 ONLY
2. 3U3 anywhere in a chain is impossible

TABULATION OF ALL POSSIBLE CASES

R	S	U-S	Name	Structure			Comments	
1	0	3	Benzene					
2	0	7	Dibenzene	01	==>	3U4		
				10	=	01		
	1	6		00	==>	3S3		
3	0	11	Tribenzene	002	==>	3U3U5	IMPOSSIBLE	# 1 & 2
				011		3U4U4	A1	
				020		3U5U3	B1	
				101		4U3U4	B4	
				110	=	011		
				200	=	002		
	1	10		001		3U3S4	IMPOSSIBLE	# 1 & 2
				010		3U4S3	B2	
				100		4U3S3	A2	
	2	9		000		3S3S3	B5	
4	0	15	Tetra-	0003	==>	3U3U3U6	IMPOSSIBLE	# 1 & 2
			benzene	0012		3U3U4U5	IMPOSSIBLE	# 1 & 2
				0021		3U3U5U4	IMPOSSIBLE	# 2
				0030		3U3U6U3	IMPOSSIBLE	# 2
				0102		3U4U3U5	IMPOSSIBLE	# 1
				0111		3U4U4U4	AA1	
				0120		3U4U5U3	BA1	
				0201		3U5U3U4	BB1, DB1	
						cis & trans respectively		
				0210	=	0120		
				0300	=	0030		
				1002		4U3U3U5	IMPOSSIBLE	# 1 & 2
				1011		4U3U4U4	BA6	
				1020	=	0201		
				1101	=	1011		
				1110	=	0111		
				1200	=	0021		
				2001	=	1002		
				2010	=	0102		
				2100	=	0012		
				3000	=	0003		

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4   1   14          0002 ==> 3U3U3S5    IMPOSSIBLE  # 1 & 2
                             3U3S3U5    IMPOSSIBLE  # 1 & 2
                             3S3U3U5    IMPOSSIBLE  # 1 & 2
                     0011    3U3U4S4    IMPOSSIBLE  # 1 & 2
                             3U3S4U4    IMPOSSIBLE  # 2
                             3S3U4U4    AA2
                     0020    3U3U5S3    IMPOSSIBLE  # 2
                             3U3S5U3    IMPOSSIBLE  # 2
                             3S3U5U3    BA3
                     0101    3U4U3S4    IMPOSSIBLE  # 1
                             3U4S3U4    BA4
                             3S4U3U4    BB4, DB4
                             cis & trans respectively
                     0110    3U4U4S3    BA2
                             3U4S4U3    BB3, DB3
                             cis & trans respectively
                             3S4U4U3  =  3U4U4S3
                     0200  = 0020
                     1001    4U3U3S4    IMPOSSIBLE  # 1 & 2
                             4U3S3U4    AA3
                             4S3U3U4  = 4U3U3S4 (IMPOSSIBLE)
                     1010  = 0101
                     1100  = 0011
                     2000  = 0002

4   2   13          0001 ==> 3U3S3S4    IMPOSSIBLE  # 1 & 2
                             3S3U3S4    IMPOSSIBLE  # 1 & 2
                             3S3S3U4    BA7
                     0010    3U3S4S3    IMPOSSIBLE  # 2
                             3S3U4S3    BA5
                             3S3S4U3    BB2, DB2
                             cis & trans respectively
                     0100  = 0010
                     1000  = 0001

4   3   12          0000 ==> 3S3S3S3    BB6, DB6
                             cis & trans respectively
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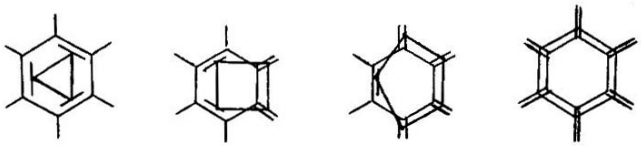


0 2 4 6

FIGURE 5

examined is an end ring, only the 3-gon and 4-gon are viable for cata-condensation. On the other hand, if we allow for either peri-condensation or for single atoms being doubly-bonded to the ring, such as =O, all four possible duals can exist. Consequently, observation 1 has been justified for all unifilar, cata-condensed polybenzenes.

Justification of observation 2 is seen by remembering that for any unifilar junction of two rings, the junction is a single bond and that an edge of the dual n-gon must be parallel to this edge. When this is done for one of the 3-gons, the only way to get the required parallel edge would be for there to exist a double bond in the second ring that was also parallel to the edge; however, such a structure would have a break in the conjugation for a two ring system (Figure

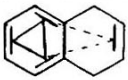
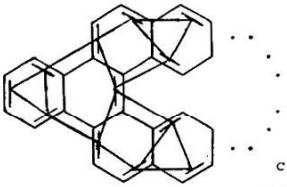


FIGURE 6

6), while an extension such as shown in Figure 7 would result in the formation of a 5-gon adjacent to the 3-gon



Is closure possible?

FIGURE 7

ASSUMING that by "closing the ring" it were possible to maintain the conjugation. Whether this is a legitimate usage of the term "cata-condensation" depends on the definition that one chooses to give to this term.[9] In any case the 3U3 combination is unattainable within the constraints of maintaining conjugation.

Before progressing to polyfilar systems of rings, one simplification for computer purposes is to subtract 3 for each ring in the system before tabulating Table 1. This allows for a simplified pencil and paper, as well as a computer, check that all possible cases have been examined.

We are now ready to extend the suggested algorithm to accomodate polyfilar cata-condensed ring systems. For this purposes we now make four additional observations and include the justifications for each. These are given in the top part

TABLE 2

POLYFILAR CATA-CONDENSED RING SYSTEMS

ADDITIONAL OBSERVATIONS

3. 2 polygons attached at edges to a triangle leave no free vertex for a spiro connection; i.e., $3(U_a,U_b,S_c)$ is impossible.
4. 2 polygons attached at vertices to a triangle leave no free edges for a unifilar connection; i.e., $3(U_a,S_b,S_c)$ is impossible.
5. 2 polygons can be attached at edges to a square only in a strictly collinear; i.e., $4(U_a,U_b,X_c)$ where X = U or S is impossible
6. 2 polygons can be attached at edges to a pentagon only in a collinear orientation, in the sense of Reference 5.

TABULATION OF ALL POSSIBLE CASES
(Note that instead of the linear notation used in Table 1, it is more convenient to use: center ring (each polyfilar rings)

R	S	U-S	Name	Structure			Comments
4	0	15	Tetra-	0(0,0,3)	=>	3(U6,U3,U3)	IMPOSSIBLE 1, 2
			benzene	0(0,1,2)		3(U5,U4,U3)	IMPOSSIBLE 1, 2
				0(1,1,1)		3(U4,U4,U4)	FB4
				1(0,0,2)		4(U5,U3,U3)	IMPOSSIBLE 1, 5
				1(0,1,1)		4(U4,U4,U3)	IMPOSSIBLE 5
				2(0,0,1)		5(U4,U3,U3)	IMPOSSIBLE 6
				3(0,0,0)		6(U3,U3,U3)	FB1
4	1	14		0(0,0,2)		3(U5,U3,S3)	IMPOSSIBLE 1, 3
						3(S5,U3,U3)	IMPOSSIBLE 1, 3
				0(0,1,1)		3(U4,U4,S3)	IMPOSSIBLE 3
						3(S4,U4,U3)	IMPOSSIBLE 1, 3
				1(0,0,1)		4(U3,U3,S4)	IMPOSSIBLE 1, 5
						4(U3,S3,U4)	IMPOSSIBLE 5
				2(0,0,0)		5(U3,U3,S3)	FB2
4	2	13		0(0,0,1)		3(U3,S3,S4)	IMPOSSIBLE 1, 4
						3(U4,S3,S3)	IMPOSSIBLE 4
				1(0,0,0)		4(U3,S3,S3)	FB3
4	3	12		0(0,0,0)		3(S3,S3,S3)	FB5

of Table 2. Note that because the reasons for impossibility in polyfilar systems also include the unifilar restrictions, these have been assigned numbers 3 through 6.

Next, instead of the linear notation which serves us so well for unifilar systems, the notation selected shall be the central ring, left parenthesis, a U or S followed by the ring size for each of the "buds", and then the right parenthesis. Furthermore, since the smallest polyfilar ring system is four rings, in the remainder of Table 2, we have determined all of the non-redundant Kekule structures of the only existent polyfilar tetrabenzene. For the computer, this means first tabulating all of the different combinations that sum to 3, 2, 1 and 0 respectively. Eliminating those that are excluded by Table 2, we obtain the five different resonance forms of FB-tetrabenzene. Note that this is corroborated by following the tedious task of following all permutations of the figure in Patterson position. The nine such permutations shown in Figure 8 are seen to have four redundancies. Consequently,

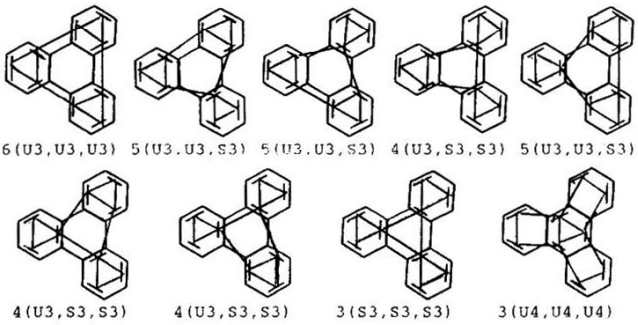


FIGURE 8

this technique generates only the constitutionally distinct Kekule structures for polyfilar cata-condensed polybenzenes.

3. PERI-CONDENSED POLYBENZENES

The extension to viable peri-condensation (Note that C-Tribenzene is peri-condensed, but is not viable; inasmuch as there is no way to allocate a conjugated system of bonds that

spans the molecule) could be undertaken in the same manner as for cata-condensation by listing all possible combinations that sum to 4R - 1 - X and then eliminating all impossible cases. The problem with this approach is: What should the symbol X mean? Note that the concept of "spiro" in the dual graph is unambiguous ONLY so long as the dual graph is either uni- or polyfilar, but NOT reticular.

To gain a greater appreciation of the problem, examine the smallest polybenzene having this form: CB-Tetrabenzene (pyrene). For each of the 6 Kekule structures, we draw in the duals (Figure 9). Note that in this four ring system, for two

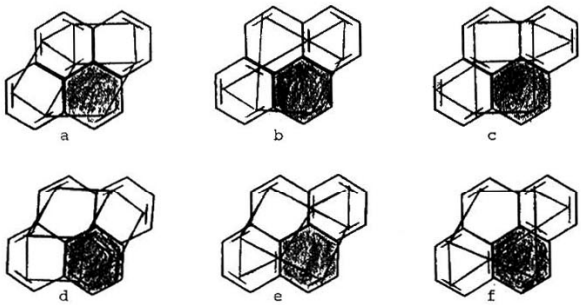


FIGURE 9

of these duals the sum of sides = 15 while for the other four the sum of sides = 14. In order to rationalize these numbers (which seem consistent with the cata-condensed tetrabenzenes), let us examine the number of double bonds emanating from a "central ring" (shaded in Figure 9). Since two vertices of this central ring are "free", the number of double bonds that could emanate from this ring is at most four. For the case of four double bonds emanating from the central ring, the dual figure using these four bonds is a pentagon, surrounded by three adjacent triangles (b of Figure 9). Next for two double bonds, these may be either together (c and e -- isomorphic by rotation about a 30° diagonal line) or separated (a). Finally, for zero double bonds emanating from the "center", the conjugation of the central ring can be either of two forms

(d and f). Note that f is isomorphic to b by rotation thru 180°, and similarly 180° rotation of d produces a. At this point, note that we can now develop a tabulation comparable to Table 2; however, we need a new set of restrictions (Table 3).

TABLE 3
TABULATION OF ALL POSSIBLE CASES FOR PYRENE

Structure	Comments
0003	Impossible since this would require six axial double bonds around a single ring; i.e, a central hexagon.
0012	Impossible since the four axial double bonds needed to form the central pentagon uniquely position the remaining double bonds (one completes the pentagon, the other three all form triangles). This is 0002.
0111	a and d of Figure 9
0002	b and f of Figure 9
0011	c and e of Figure 9
0001	Impossible since in order to have exactly two axial double bonds around "central ring", this must be on one of "end rings". Now the other end ring must have three double bonds; which can occur in two different ways both of which have already been used -- 0002 and 0011.
0000	Impossible since (a) if a double bond is between the two "central" rings, there is no way to allocate the remaining six double bonds and still maintain conjugation and (b) if a single bond is between the two central rings, this produces 0002.

One attempt at rationalization -- which works for pyrene and some other molecules -- is to note the number of multiple points (vertices common to 3 or more n-gons of the dual), M, and subtract this number from 4R; i.e., in a (and d) of Figure 9, there is only one vertex at which 3 or more of the n-gons are coincident; i.e., M = 1. Thus U = 4 * 4 - 1. In b, c (and f, e), there are two multiple-point vertices (each having exactly three coincident n-gons); thus U = 14.

Continuing now to the three viable peri-condensed pentabenzenes (DBA-, ICA- and JCA):

(a) For DBA-Pentabenzene (IUPAC name = Benzo[a]pyrene), a table comparable to Table 3 would have as a fifth n-gon either a spiro triangle or a unifilar rectangle or triangle connected to the leftmost ring in the pyrene structures shown in Figure 9. However, no formula involving U (which assumes the value of 17 twice, 18 five times and 19 twice for the nine different Kekule structures that can be formed) is evident at present.

(b) For ICA-Pentabenzene (IUPAC name = Benzo[b]pyrene), a different table comparable to Table 3 can be formulated. For the ten different Kekule structures, four have U = 17, five have U = 18 and one has U = 19; but again all would-be generalizations are forced and no simplification is evident.

(c) For JCA-Pentabenzene (perylene), on the other hand, upon examining the nine different Kekule structures, from which four different duals are created, we note that for each of these, U = 18.

4. CORONA-CONDENSED POLYBENZENES

Correlation of the results for the three viable peri-condensed pentabenzenes indicates that, in general, each separate combination of hexagons which form a peri-condensed polybenzene must be examined individually. There is, however, one combination of hexagons that seems to have a unified formula -- without regard to what value X should have. This is the class of "single-layer" corona-condensed molecules. For this class of compounds, which geometrically are represented by multiply-connected regular and dual graphs, the relevant formula is: Adding the size of the central ring of the dual to the sum of the n-gons (including the central ring) yields a characteristic number, U', which is the same for all of the Kekule structures of that molecule. For coronene, in which the values for U range from 24 through 27, U' is always = 30. Figure 10 and Table 4 show these results for the twenty different Kekule structures of coronene. Similarly, Figure 11 show a representative example of the next two corona-condensed molecules that can be formed. Note for each of these the

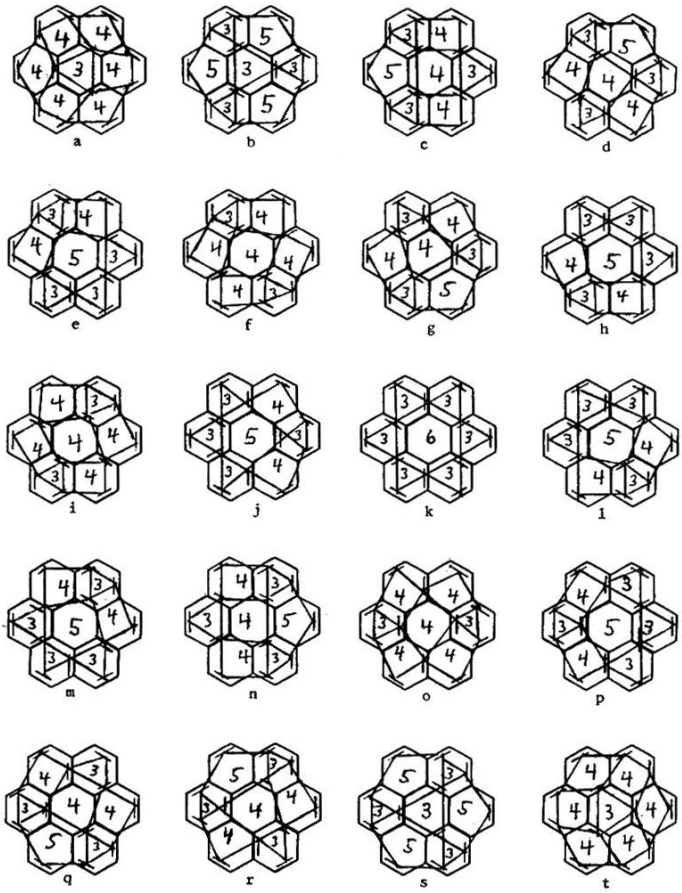


FIGURE 10

value of U' = 6(R-1), where the "central ring" of this multi-connected system is NOT counted in the value of R. For coronene this means R = 6, NOT 7.

The nomenclature for a corona-condensed polybenzene will be akin to that used for polyfilar systems; namely, list first the central ring and then inside parentheses list -- in sequence -- the connection mode (U or S) and the ring size, separated by commas. To get a canonical name, start from the largest ring and progress in the direction such that the next largest ring appears as soon as possible (See Table 4).

TABLE 4

NOMENCLATURE (& SYMMETRIES) OF KEKULE STRUCTURES OF CORONENE

a.	3(U4,U4,U4,U4,U4,U4)	l.	5(S4,U3,U3,S3,S3,S3)
b.	3(U5,U3,U5,U3,U5,U3)	m.	60° rotation of e
c.	4(U5,U3,U4,S3,S4,U3)	n.	180° rotation of c
d.	240° rotation of c	o.	60° rotation of f
e.	5(S4,U3,U4,S3,S3,S3)	p.	300° rotation of e
f.	4(U4,S4,U3,U4,S4,U3)	q.	60° rotation of c
g.	120° rotation of c	r.	300° rotation of c
h.	120° rotation of e	s.	Vertical reflection of b
i.	120° rotation of f	t.	Vertical reflection of a
j.	240° rotation of e		
k.	6(S3,S3,S3,S3,S3,S3)		

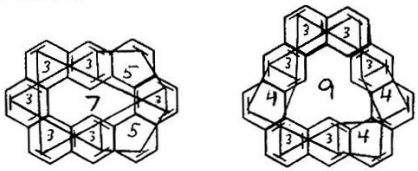


FIGURE 11

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