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Enumeration and Classification of Coronoid Hydrocarbons. 10. Double Coronoids

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A multiple coronoid is a polyhex with more than two corona holes. Double coronoids with two holes are treated most extensively. They are classified into (a) those obtained by additions of hexagons, (b) primitive, (c) nonprimitive basic, and (d) nonbasic extras. This classification is important under the computer-aided specific generation of the double coronoids. A full account is given for the numbers of nonisomorphic double coronoids with the number of hexagons (h) up to 16. Among the 1618 systems with $h = 16$, the 64 systems under the categories (b), (c), and (d) are described extensively, and their forms are depicted. Machine-computed Kekulé structure counts are reported for many double coronoids, and for some of them also an analytical solution according to the method of fragmentation is shown. Some features of triple coronoids (three holes) are included.

INTRODUCTION

A polyhex is a geometrical object consisting of congruent regular hexagons in a plane. According to a strict definition this system of hexagons is connected, and any pair of hexagons in it either share exactly one edge, or they are disjoint. A coronoid (system) is a polyhex with a (corona) hole of the size of more than one hexagon. For general references to treatments of benzenoids (polyhexes without holes) and coronoids we cite some monographs.[1–6]

Benzenoids and coronoids have chemical counterparts in a subset of polycyclic conjugated hydrocarbons, that is in polyhex hydrocarbons. Two of the molecules corresponding to coronoids have been synthesized, viz., cyclo[*d.e.d.e.d.e.d.e.d.e.d.e*]dodecakisbenzene or kekulene[7] and cyclo[*d.e.d.e.e.d.e.d.e.e*]decakisbenzene.[8] They both belong to the class of cycloarenes.[9] The corresponding coronoid systems are classified as primitive coronoids.[10] The most famous of these compounds is $C_{48}H_{24}$, kekulene; the same name is used also about the primitive coronoid system, which is depicted in Figure 1 (left).

Kekulene is a rather stable chemical compound, characterized as "greenish-yellow microcrystals", "with its extreme insolubility in solvents of all kinds".[7] It should be noted that the molecule actually has a cavity, into which carbon–hydrogen bonds are pointing, this being a characteristic feature of cycloarenes. Yet the steric hindrances[11] are not serious enough to prevent the molecule from being basically planar.[12,13] It can be predicted that the regular hexagonal hexabenzokekulene ($C_{72}H_{36}$), as is depicted in Figure 1 (right), would be extraordinarily stable chemically.[14,15] The coronoid system belongs to all-coronoids, defined in the same way as all-benzenoids[16] (or fully benzenoids[17]). In our case (Figure 1) the all-coronoid has $2^{12} = 4096$ Kekulé structures with 12 aromatic sextets[17] each out of the total number of 7776.

Theoretically there should be no objection against the possibility to synthesize the "double kekulene" $C_{92}H_{38}$ and its extension to an all-coronoid $C_{124}H_{54}$; see Figure 2. These two systems, having two corona holes each, are called double coronoids. A coronoid with one hole should then be termed more strictly a single coronoid.

The smallest (single) coronoid has eight hexagons, while the smallest double coronoid has 13. These two systems are shown in Figure 3 together with their extensions to all-coronoids. However, one should not be misled to believe that every coronoid system can be converted to an all-coronoid in this way; the cases of Figures 1–3 are rather exceptional.

We shall (as usual) identify the number of hexagons of a polyhex (benzenoid or coronoid) by the symbol h. The Kekulé structure count (or number of Kekulé structures) is designated by K. Hence we also speak about the K number.

The $h = 8$ system of Figure 3 was depicted, perhaps for the first time, by Ege and Vogler,[18,19] and later by several others in connection with different theoretical works.[10,20–27] The $h = 12$ system of Figure 3 is the smallest all-coronoid. The possibility to construct what we call all-coronoids was pointed out already by Polansky and Rouvray,[28] while the particular smallest system of this kind was depicted by Bergan et al.,[29] who also gave its Kekulé structure count (see Figure 3). Hydrocarbons corresponding to the $h = 8$ and $h = 12$ coronoids referred to above are not likely to be synthesized because of severe steric hindrances inside the cavities of these (hypothetic) molecules. However, it should be clear after the above description that these systems are of great importance in theoretical and mathematical chemistry. The same can be said about the two double coronoids in Figure 3. The bottom-left ($h = 13$) system is the absolutely smallest double coronoid, while the bottom-right ($h = 17$) system is the smallest double all-coronoid. The former ($h = 13$) of these systems was mentioned, probably for the first time, by Dias,[30] and later by Brunvoll et al.,[10] who also gave the K number of this coronoid.

A large amount of work has been published on the single coronoids. A complete list of references would be too voluminous to be cited here, but the reader is referred to some additional references in the following. With regard to the double coronoids, however, the amount of work done is much more modest. In a recent theoretical work of considerable significance, Hall[26] made allowance for more than one corona hole of a polyhex and referred to the number of holes as the

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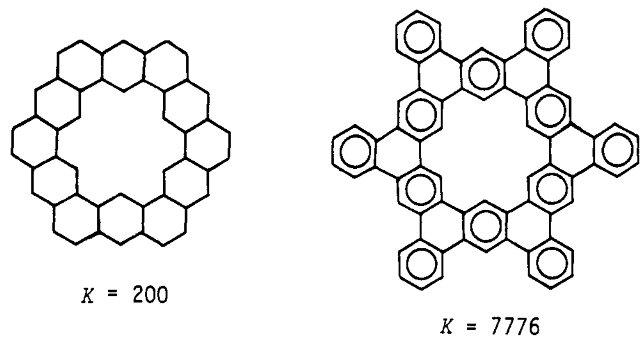


Figure 1. Kekulene (left) and a hexabenzokekulene (right). Kekulê structure counts (K) are given.

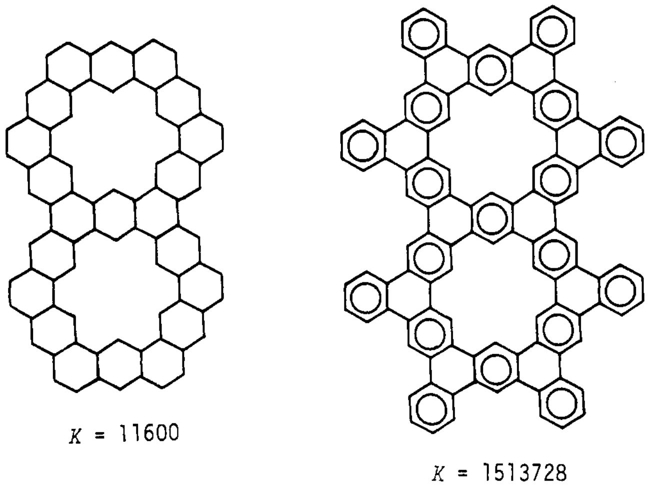


Figure 2. Two double coronoids. The right-hand system is an all-coronoid. K numbers are given.

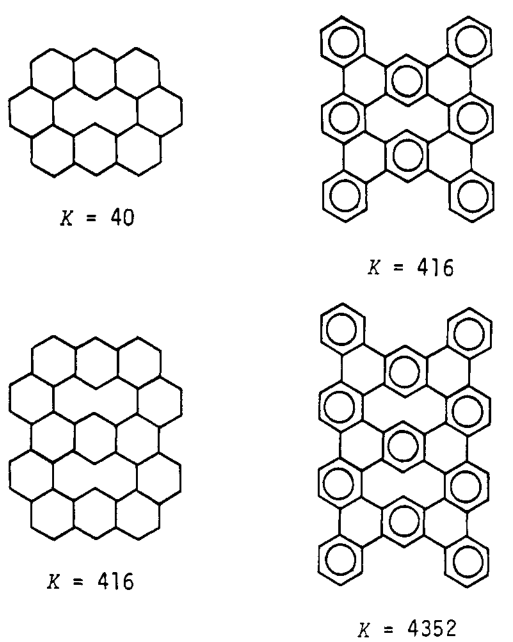


Figure 3. Four coronoid systems. Those in the right-hand column are all-coronoids. K numbers are given. Two of the systems have the same K number "by accident".

genus (g). We shall refer to such systems as multiple coronoids. A coronoid of genus g would therefore be a g-tuple coronoid in our terminology. With regard to the Kekulê structure counts of multiple coronoids, the K numbers have been reported for some isolated systems.[10,31] Furthermore, combinatorial K formulas for certain classes of multiple coronoids ("perforated rectangles" and related systems) have recently been produced.[32,33] Some of these formulas somehow explain the coincident K numbers for two of the systems of Figure 3. The first enumeration of double coronoid systems, achieved by Knop et al.,[34] was actually the work which inspired us to the present investigations.

Table I. Numbers of Graphs Corresponding to Chemical Isomers of Some Single Coronoids

h	formula	number
8	$C_{32}H_{16}$	1[a]
9	$C_{36}H_{18}$	3[a]
10	$C_{40}H_{20}$	15[b]
11	$C_{44}H_{22}$	62[b]
12	$C_{48}H_{24}$	312[c]
13	$C_{52}H_{26}$	1435[c]
14	$C_{56}H_{28}$	6785[d]

[a] Dias.[24] [b] Brunvoll et al.[10] [c] Balaban et al.[35] [d] He et al.[36]

Table II. Numbers of Polyhexes with Different Numbers of Corona Holes

	g (genus, no. of holes)		
h	0	1	2
8	1 435[a]	1[f]	
9	6 505[a]	5[f]	
10	30 086[a]	43[g]	
11	141 229[b]	283[h]	
12	669 584[c]	1 954[h]	
13	3 198 256[d]	12 363[i]	1[l]
14	15 367 577[d]	76 283[j]	11[l]
15	74 207 910[d]	453 946[k]	149[k]
16	359 863 778[e]	2641 506[e]	1618[e,m]

[a] Knop et al.;[44] Trinajstić et al.[45] [b] Stojmenović et al.[46] [c] He et al.[36] [d] Nikolić et al.[42] [e] Trinajstić.[47] [f] Knop et al.[38] [g] Knop et al.[25] [h] Brunvoll et al.[10] [i] Cyvin et al.[31] [j] Cyvin et al.[48] [k] Brunvoll et al.[43] [l] Knop et al.[34] [m] Present work.

The main subject of the present work is the double ($g = 2$) coronoids. A computer-aided specific generation and enumeration furnishes a substantial supplement to the previous data.[34] Detailed classifications of the generated systems are performed according to several different principles. Also the Kekulê structure counts are considered. Finally, a short account on triple ($g = 3$) coronoids is given.

SURVEY OF ENUMERATIONS

Previous Results. The first enumeration of (single) coronoids is probably due to Dias,[24] who reported numbers of the chemical isomers $C_{32}H_{16}$, $C_{36}H_{18}$, $C_{40}H_{20}$, $C_{44}H_{22}$, and $C_{48}H_{24}$. The chemical formulas $C_{4h}H_{2h}$ are to be associated with the catacondensed single coronoids. As such they have been enumerated[10,35,36] up to $h = 14$ with the results shown in Table I. It is emphasized that the coronoid systems (chemical graphs) are enumerated, not the chemical compounds. The numbers do not include helicenic (nonplanar) systems. We find discrepancies[37] with the Dias numbers[24] for $h > 9$.

In most of the enumerations of polyhexes the number of hexagons (h) was taken as the leading parameter. We give references to some of the works which contain data on coronoids.[2,10,25,31,34-36,38-43] In additional works (not cited here for the sake of brevity) special classes of single coronoids have been enumerated, considering specific symmetries and/or other characteristics.

Overall Results. Table II shows the available data for numbers of polyhexes with different numbers of holes. The $g = 0$ systems (without holes) originate from different places.[36,42,44-47] The corresponding data for $h < 8$ (where no coronoids exist) are available from still more places; see, e.g., the quotations of the consolidated report by 14 authors.[35]

Table II includes the total numbers of single ($g = 1$) and double ($g = 2$) coronoids. The number 1618 for double coronoids with $h = 16$ was obtained in the present work in a completely different way from the computerized analysis which

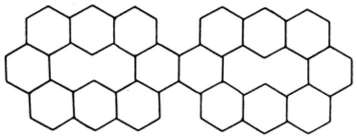


Figure 4. A catacondensed double coronoid, which is not primitive. It is composite.

was running parallel to it.[47] The smallest triple ($g = 3$) coronoid occurs at $h = 18$. Dias[30] identified one such system as a $C_{68}H_{28}$ compound. We have produced four triple coronoids with $h = 18$. Two of them (including the one of Dias[30]) are $C_{68}H_{28}$ isomers, while two others are associated with $C_{67}H_{27}$. The forms are specified at the end of this paper.

BASIC PRINCIPLES OF ENUMERATION

Throughout this work the number of hexagons, viz., h, is taken as the leading parameter. Helicenic systems are excluded.

The previously employed computer programs[10,49,50] were adapted to the generation and enumeration of double coronoids. The systems were obtained by *specific generation*.[49] This contrasts the methods of Knop et al.[34] and Nikolić et al.[42] (both works with Trinajstić as senior author), who obtained the desired systems by *recognition*[49] from whole sets of polyhexes with given h values. This distinction seems important to be stressed here. It is of course of great interest to generate and enumerate all polyhexes with a given h, but as a method for studying the double coronoids exclusively it is hopelessly inefficient. Thus, for instance, the 11 double coronoids have to be recognized among a totality of 15 443 871 systems (cf. Table II).

As a basic principle we generate the double coronoids with $h + 1$ hexagons by (a) adding one hexagon in all possible (or some selected) positions to all double coronoids with h hexagons and (b) supplement the set with all relevant double coronoids with $h + 1$ hexagons which can not be generated in the former way.

Certain systems called *basic* must always be added as extra systems under (b), but it may also be necessary to add nonbasic systems. Yet it should be clear that a thorough treatment of the class of basic double coronoids is warranted.

DEFINITIONS AND SOME TOPOLOGICAL PROPERTIES OF BASIC SINGLE AND DOUBLE CORONOIDS

Primitive Coronoids. The definition of *primitive* single coronoids[6,10,27] seems by now to be well established. Such a system consists of a single chain in a macrocyclic arrangement. In terms of hexagon modes:[5] In a primitive single coronoid any hexagon is in the mode A_2 or L_2 (which may be lacking). In consequence these systems are *catacondensed* coronoids. That is to say that they have no internal vertices. An internal vertex is a vertex (of degree three) shared by three hexagons. The $h = 12$ and $h = 8$ systems of Figures 1 and 3, respectively, are primitive single coronoids. We shall now use the above concepts in a precise definition of primitive double coronoids.

(A) A primitive double coronoid is catacondensed. (B) It consists of two primitive single coronoids which share some hexagons. Under these conditions the sharing of only one hexagon is impossible.

We find that a primitive double coronoid has (a) a number of hexagons in the modes A_2 and L_2 (where L_2 may be lacking) and (b) exactly two (bridging) hexagons in the mode A_3. The $h = 21$ and $h = 13$ systems of Figures 2 and 3, respectively, are primitive double coronoids.

Notice that the above description of hexagon modes is not sufficient as a definition of a primitive double coronoid. Figure 4 shows an example where the system satisfies the description but is not a primitive coronoid according to the strict definition. A system like this is called *composite* because it may be separated into two polyhexes (in this case two primitive single coronoids) by cutting along one edge. A primitive coronoid is never composite.

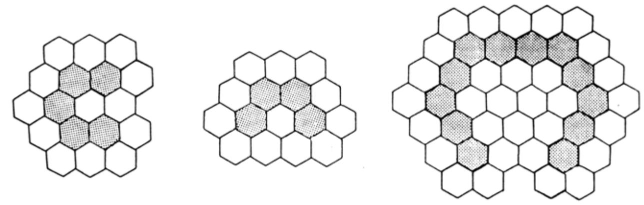


Figure 5. Three nonprimitive basic single coronoids. The corona holes are drawn as grey hexagons.

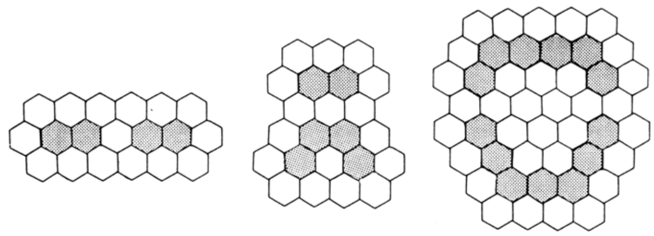


Figure 6. Three nonprimitive basic double coronoids. The corona holes are drawn as grey hexagons.

There is a one-to-one correspondence between a primitive coronoid and a corona hole or, in the case of double coronoids, a constellation of the two holes. However, many shapes of a corona hole, and constellations of holes, cannot serve as corona holes for primitive coronoids.

The primitive coronoids form a subclass of basic coronoids.

Nonprimitive Basic Coronoids. A listing of basic coronoids is the same as a listing of corona holes or, in the case of double coronoids, constellations of holes.

Let us first consider the single coronoids. A basic single coronoid is the smallest coronoid compatible with a given hole. This definition also covers the primitive (single) coronoids. Some nonprimitive basic single coronoids are shown in Figure 5. They may be found by circumventing the corona hole and, if necessary, filling out a created cavity by hexagons. The requirement of filling out a cavity should be clear by inspecting the right-hand system of Figure 5. The left-hand system of the figure shows that a nonprimitive basic coronoid may be catacondensed. Now a definition of basic double coronoids follows in terms of a prescription of how they can be constructed from a given constellation of two holes (viz., a given pair of holes in a given position).

(A) Construct the basic (primitive or nonprimitive) single coronoid around each of the two holes. (B) Take these two coronoids together if they share some hexagons. Then a basic double coronoid exists and may already be this union of coronoids. (C) If necessary, fill out a created cavity by hexagons.

This definition also covers the primitive double coronoids. It should be noticed, however, that a merging of two primitive single coronoids may result in a nonprimitive basic double coronoid. This situation is illustrated by the left-hand system of Figure 6. The right-hand system of the figure exemplifies the necessity of filling out a cavity as described under point (C) above.

The above definition implies that a basic double coronoid may not exist for a given hole constellation, if the two holes are too far apart from each other. Figure 4 shows already one example. The two single coronoids may also be condensed in a way as depicted in Figure 7.

If a basic coronoid exists for a given constellation of two holes, then it is the unique smallest basic double coronoid

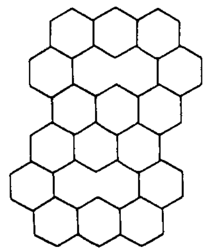


Figure 7. A double coronoid which is not basic.

compatible with this constellation.

GENERATING BASIC DOUBLE CORONOIDS

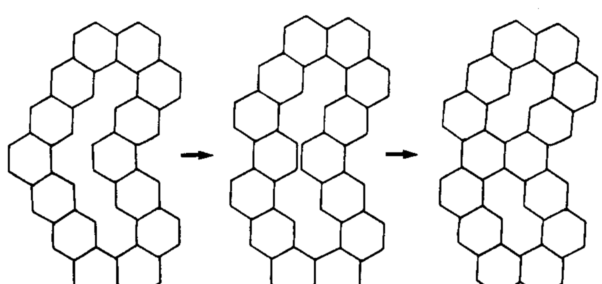
Introduction. The basic double coronoids for h = 13–16 were generated by hand (without computer aid) according to different principles. The procedures may be characterized as systematic trial and error. It was accomplished by taking advantage of the great knowledge which has been accumulated on primitive single coronoids.[27] Different approaches along these lines were employed in order to check the results.

Furthermore, a quite different combinatorial approach was applied independently. It is described under General Algorithm. It is supposed that it would be convenient for computer programming.

Thirteen-Hexagon System. The unique double coronoid with h = 13 is found in Figure 3 (bottom-left). It is a primitive double coronoid. The system can be interpreted in either of the following two ways. (1) A primitive single coronoid with 12 hexagons and one hexagon forming a bridge; let this interpretation be coded as 12+1. (2) Two primitive single coronoids with 8 hexagons each, having three hexagons in common; in coded form say 8+8–3.

It should be pointed out that we are not trying to devise a chemical nomenclature; the codings are frequently ambiguous when it comes to the identification of a hydrocarbon.

Fourteen-Hexagon Systems. In the case of h = 14 one has the possibilities 12+2, 13+1, and 14+0 for the basic double coronoids. The last code, viz., 14+0, indicates a "no-hexagon" bridge, which may be established for helicenic quasi-coronoids of the primitive-coronoid type. The helicenic system itself may be obtained from a primitive single coronoid by a modification of the hexagon chain as exemplified below for the last (bottom-right) system of Figure 8:



The complete set of basic double coronoids, which are generated in the indicated way, are collected in Figure 8. It is clear that only the h = 8 and h = 9 primitive single coronoids can be involved, and the latter system only in the combination 9+8–3, which is the alternative code for the bottom-left system of Figure 8. Otherwise we have 8+8–2.

Fifteen-Hexagon Systems. For h = 15 the actual codes are 13+2, 14+1, and 15+0. In order to generate the basic double coronoids, the pictures[27] of all primitive single coronoids with h = 13 (12 systems), h = 14 (40 systems), and h = 15 (68 systems) were inspected. Figure 9 shows the three 13+2 systems, which are composed according to the codes 9+8–2

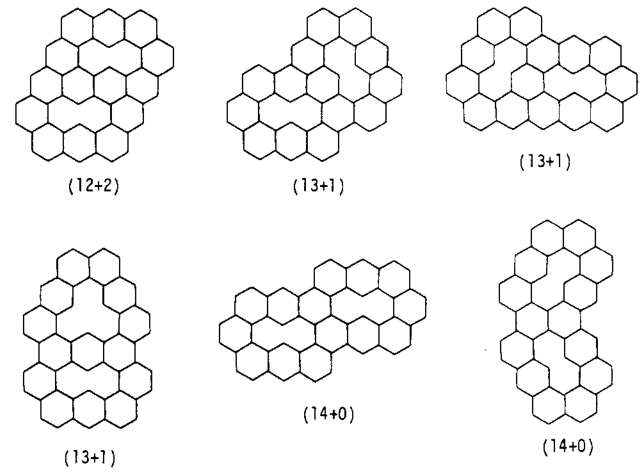


Figure 8. Six basic double coronoids with h = 14: top row, nonprimitive; bottom row, primitive. Codes are given.

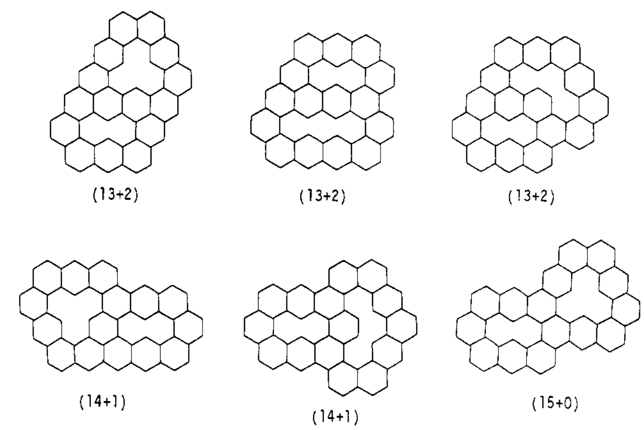


Figure 9. Six examples of basic double coronoids with h = 15: the two last ones (bottom row), primitive; the other, nonprimitive. Codes are given.

and 10+8–3 twice. Eleven 14+1 systems were deduced: four primitive composed as 9+9–3 and 10+8–3 three times; seven nonprimitive as 8+8–1 four times and 9+8–2 twice. Two examples are found in Figure 9, and an additional example in Figure 6. Finally there is only one possible system of 15+0, which has the alternative code 9+8–2; cf. Figure 9.

Sixteen-Hexagon Systems. When proceeding to higher h values, it must be assured that the same procedure as outlined above can be used without invoking nonprimitive basic single coronoids. We found that h = 16 is the last instance where the procedure works: no systems will be missed by considering the codes 14+2, 15+1, and 16+0, where the first numbers symbolize primitive single coronoids. Two examples of each of the two first types are depicted in Figure 10, one primitive and one nonprimitive. For 16+0 only primitive double coronoids can be constructed; one of them is found in Figure 10.

For the 16+0 type in particular, altogether eight systems could be constructed by inspecting the forms of the 192 primitive single coronoids with 16 hexagons[27,35] (and none from the remaining 151 basic coronoids). Pictures of the 192 forms have not been published but are available as screen displays from a suitable computer program. The same answer (eight systems) was obtained easier by making use of the fact that these systems only can be composed as 10+8–2, which gave seven systems, or 9+9–2 resulting in one system.

The first (top-left) example of Figure 10 is a borderline case inasmuch as it may be generated from a nonprimitive basic single coronoid with 15 hexagons by adding one bridging hexagon; let us symbolize this interpretation by 15′+1. But,

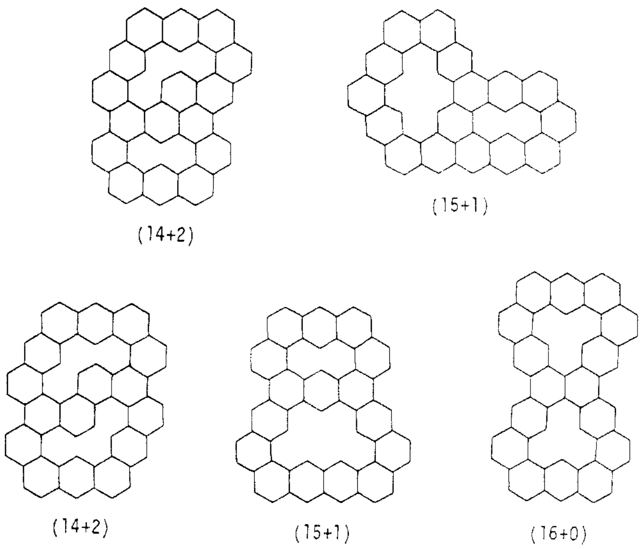
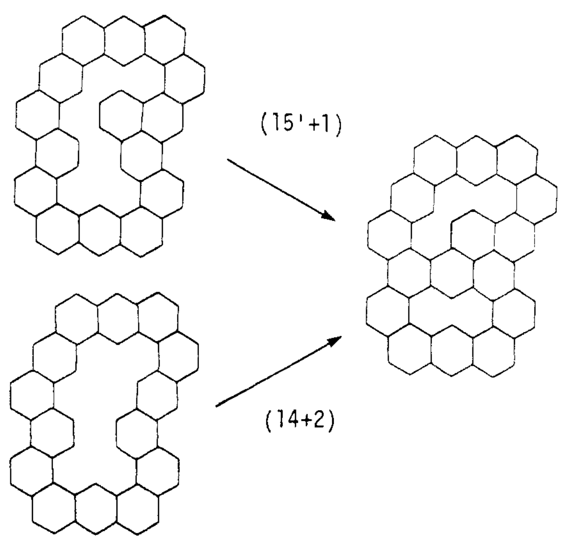


Figure 10. Five examples of basic double coronoids with h = 16: top row, nonprimitive; bottom row, primitive. Codes are given.

as indicated in the figure, it is also obtained as 14+2. For the sake of clarity we illustrate these two schemes as



The alternative code is unambiguously 10+8−2. The h = 17 system of Figure 6, on the other hand, must be coded as 16′+1. Its alternative code we shall write 12′+8−3. This is one of the smallest (h = 17) systems where nonprimitive basic single coronoids must be invoked in the generation according to the outlined principles.

Table III. Numbers of Basic Double Coronoids

h	13	14	15	16
8+8−x	1	5	4	
9+8−x		1	5	3
9+9−x			1	3
10+8−x			5	30
10+9−x				4
11+8−x				9
10+10−x				2
12+8−x				1

Table IV. Numbers of Basic Double Coronoids, Distributed into Different Classes and Symmetry Groups

h	type[a]	Δ	D_{2h}	C_{2h}	C_{2v}	C_s	total
13	prm	0	1	0	0	0	1
14	prm	0	0	1	2	0	3
	np	0	0	1	0	0	1
	o	1	0	0	0	2	2
15	prm	0	1	0	1	3	5
	np	0	1	1	1	2	5
	o	1	0	0	0	5	5
16	prm	0	2	1	1	13	17
	np	0	0	1	0	9	10
	o	1	0	0	0	24	24
	o	2	0	0	0	1	1

[a] Abbreviations: np, normal pericondensed; o, non-Kekuléan; prm, primitive.

Altogether we deduced for the h = 16 basic double coronoids, 3 primitive and 15 nonprimitive systems of 14+2; 6 primitive and 20 nonprimitive of 15+1; and finally 8 primitive systems of 16+0.

The forms of the 52 basic double coronoids are depicted (as black silhouettes) in three figures: Figure 11, primitive (which are Kekuléan); Figure 12, nonprimitive Kekuléan; Figure 13, non-Kekuléan (which are nonprimitive). By definition a *Kekuléan* polyhex possesses Kekulé structures, which a *non-Kekuléan* does not.

General Algorithm. The basic double coronoids were also generated by an algorithm independently of the above deductions. It is a purely combinatorial approach, where two given corona holes are placed in all possible ways with respect to each other and at appropriate distances. Figures 14–16 show these constellations for the two smallest holes: two naphthalenes (Figure 14), phenalene and naphthalene (Figure 15), and two phenalenes (Figure 16). Notice that the number of hexagons (h) is not constant in each of the figures. One has h = 16 − x, h = 17 − x, and h = 18 − x in the three cases, respectively. Here x = 1, 2, or 3. In terms of codes the corresponding types are 8+8−x, 9+8−x, and 9+9−x, respectively.

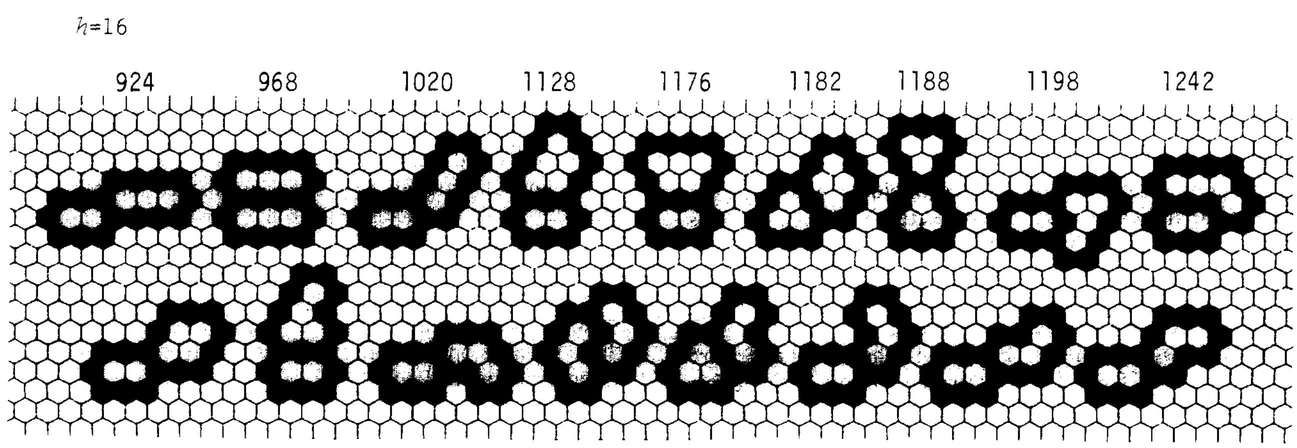


Figure 11. All nonisomorphic primitive double coronoids for h = 16. K numbers are given.

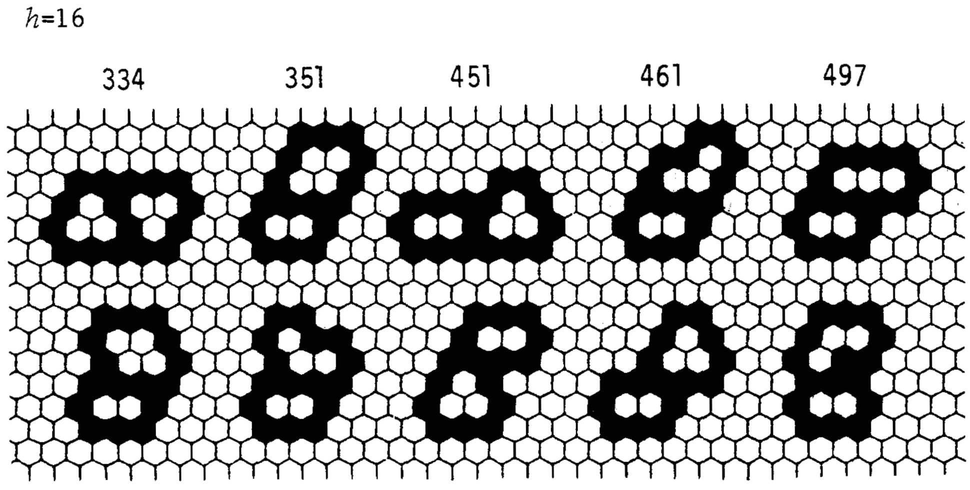


Figure 12. All Kekuléan nonprimitive basic double coronoids for $h = 16$. K numbers are given.

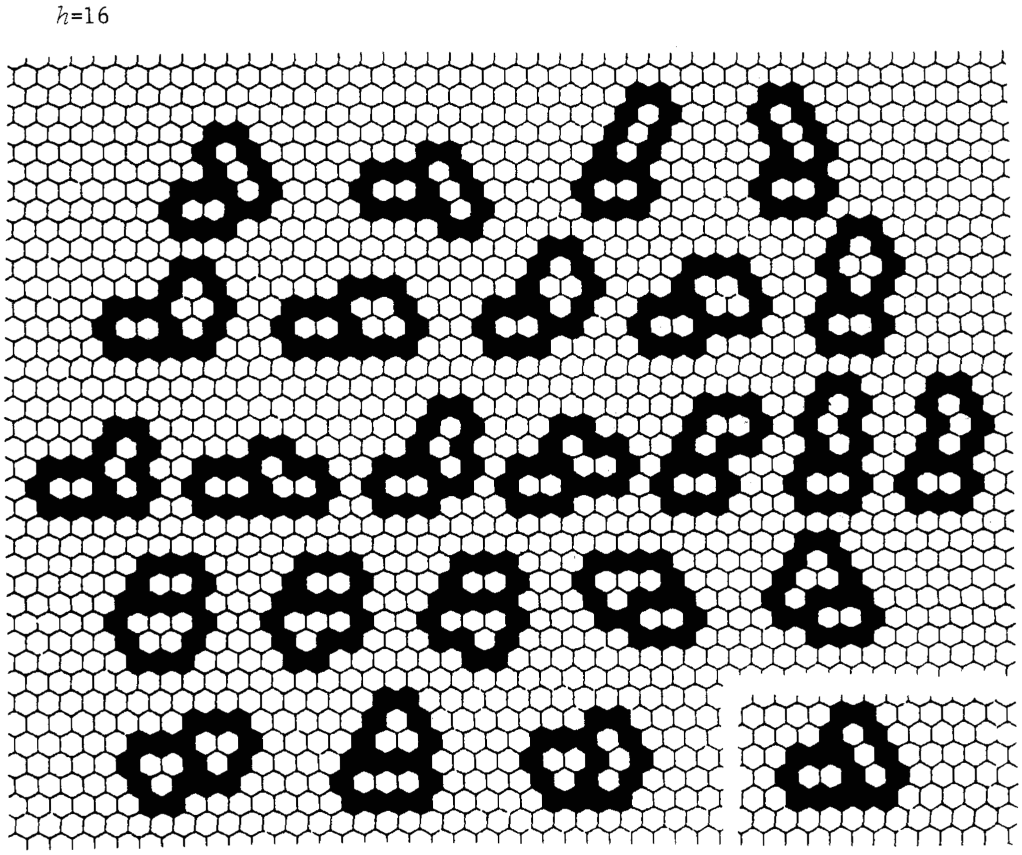


Figure 13. All non-Kekuléan (nonprimitive) basic double coronoids for $h = 16$. Δ values are given.

Table III gives a survey of the numbers of basic double coronoids with different codes (as explained above) for h = 13–16. The total numbers of the basic systems are 1, 6, 15, and 52, respectively.

For $h = 16$ in particular we have to take into account the pairs of holes as shown in Figure 17 (only one constellation for each pair is depicted).

Survey. The numbers of all (nonisomorphic) basic double coronoids for $h \leq 16$ are surveyed in Table IV. They are classified according to different schemes, which have been defined previously[5,6,35] and found to be useful. For the sake of convenience, we repeat: Δ (the color excess) is the absolute magnitude of the difference between the numbers of black and white vertices. It is also the absolute magnitude of the difference between the numbers of peaks and valleys. All Kekuléan polyhexes have $\Delta = 0$. In Table IV all the Kekuléan systems are *normal* in the sense as opposite to essentially disconnected (see below). They are divided into primitive (prm), which are catacondensed, and normal pericondensed (np). By definition a *pericondensed* polyhex has one or more internal vertices. All non-Kekuléan systems are pericondensed. Those of Table IV have $\Delta > 0$ and are therefore *obvious* non-Kekuléans in contrast to the *concealed* non-Kekuléan systems (see below).

NONBASIC EXTRA DOUBLE CORONOIDS

The general algorithm of the preceding paragraph may also be used to generate the nonbasic double coronoids with h hexagons which can not be obtained by additions of one

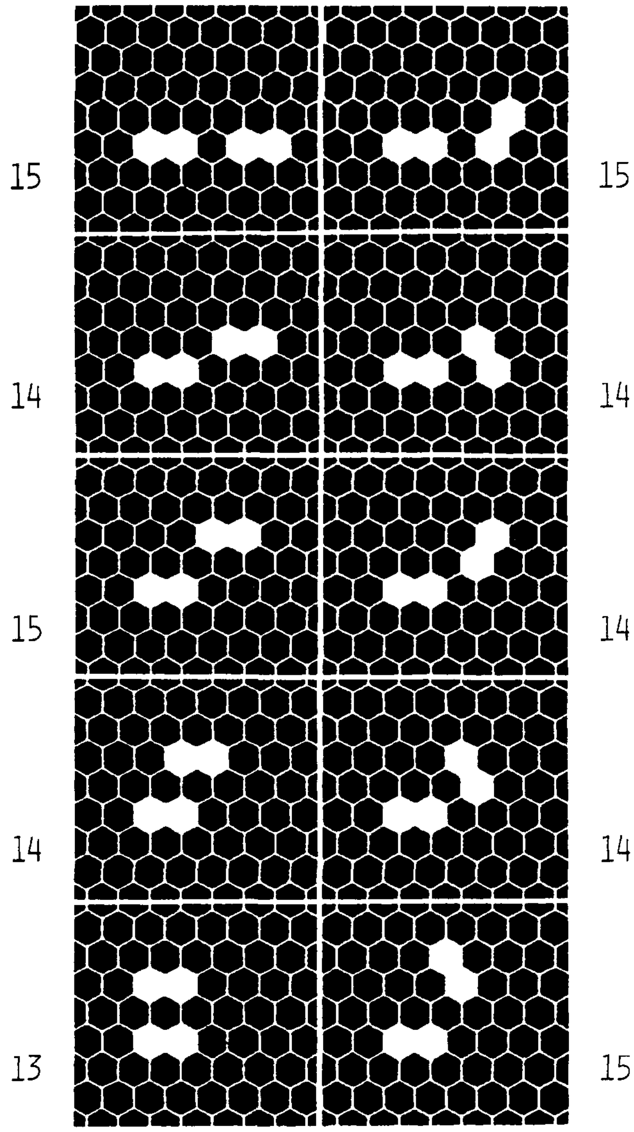


Figure 14. All (nonisomorphic) constellations of two naphthalene holes which correspond to basic double coronoids. The values of $h = 8+8-x$ are given.

hexagon to the double coronoids with $h - 1$ hexagons. This problem occurs for the first time at $h = 16$. In this case it is clear that only the constellations of two naphthalene holes are of interest. Figure 18 shows the complete scheme. Among the corresponding double coronoids we find four composite systems (cf. Figure 4) and eight condensed (cf. Figure 7). The numbers of these 12 systems, classified according to symmetry, are as follows: 1 (D_{2h}) + 5 (C_{2h}) + 1 (C_{2v}) + 5 (C_s). For the sake of clarity and for further information the 12 systems in question are shown in Figure 19.

GENERATION AND ENUMERATION OF NONBASIC DOUBLE CORONOIDS

All the (nonisomorphic) double coronoids were generated by computer aid for $h \leq 16$ following the principles outlined above. They are the (a) basic systems, (b) systems obtained by adding hexagons, one at a time, to the basic systems, and (c) the extras described in the preceding section. No additions are permitted into the corona holes. Table V gives a survey of the numbers. The Δ values are given (as in Table IV). The nonbasic systems (Table V) are classified according to the neo scheme,[5,6,35] which refers to normal (n), both catacondensed and pericondensed; essentially disconnected (e); and non-Kekuléan (o) systems. By definition an *essentially disconnected* polyhex (which is Kekuléan) possesses fixed bonds. A fixed bond is single or double at the same position in all Kekulé structures. All essentially disconnected polyhexes are pericondensed.

Table V. Numbers of Nonbasic Double Coronoids, Distributed into Different Classes and Symmetry Groups

h	type[a]	Δ	D_{2h}	C_{2h}	C_{2v}	C_s	total
14	n	0	0	0	1	2	3
	o	1	0	0	0	2	2
15	n	0	1	3	8	48	60
	e	0	0	1	1	0	2
	o	1	0	0	2	60	62
	o	2	0	0	1	9	10
16	n	0	1	21	29	574	625
	e	0	0	3	3	20	26
	o	1	0	0	5	741	746
	o	2	0	0	4	155	159
	o	3	0	0	0	10	10

[a] Abbreviations: e, essentially disconnected; n, normal; o, non-Kekuléan.

Table VI. Numbers of Double Coronoids with Specific Sets of Hole Constellations

h	h value of the starting systems: 13	14	15	16
13	1			
14	5	6		
15	56	78	15	
16	421	891	242	64
17	3 128	7 759	2 821	1 209
18	20 929	59 619	25 431	14 894

Table VII. Numbers of Double Coronoids Derived from the $h = 13$ Basic System

h	type[a]	Δ	D_{2h}	C_{2h}	C_{2v}	C_s	total
13	n	0	1	0	0	0	1
14	n	0	0	0	1	2	3
	o	1	0	0	0	2	2
15	n	0	1	3	6	18	28
	e	0	0	1	1	0	2
	o	1	0	0	1	22	23
	o	2	0	0	1	2	3
16	n	0	0	0	10	171	181
	e	0	0	0	0	10	10
	o	1	0	0	0	197	197
	o	2	0	0	1	31	32
	o	3	0	0	0	1	1
17	n	0	4	22	43	1 165	1 234
	e	0	0	4	4	104	112
	o	0	1	0	0	0	1
	o	1	0	0	7	1 468	1 475
	o	2	0	0	6	285	291
	o	3	0	0	1	14	15
18	n	0	0	0	67	7 447	7 514
	e	0	0	0	4	988	992
	o	0	0	0	0	2	2
	o	1	0	0	2	10 042	10 044
	o	2	0	0	4	2 217	2 221
	o	3	0	0	0	155	155
	o	4	0	0	1	0	1

[a] Abbreviations: see footnote a, Table V.

DOUBLE CORONOIDS WITH SPECIFIC HOLE CONSTELLATIONS

Additional information is gained by considering specifically the double coronoids with given constellations of the corona holes.

In the first place the additions of hexagons to the unique $h = 13$ double coronoid (see Figure 3) were executed. The

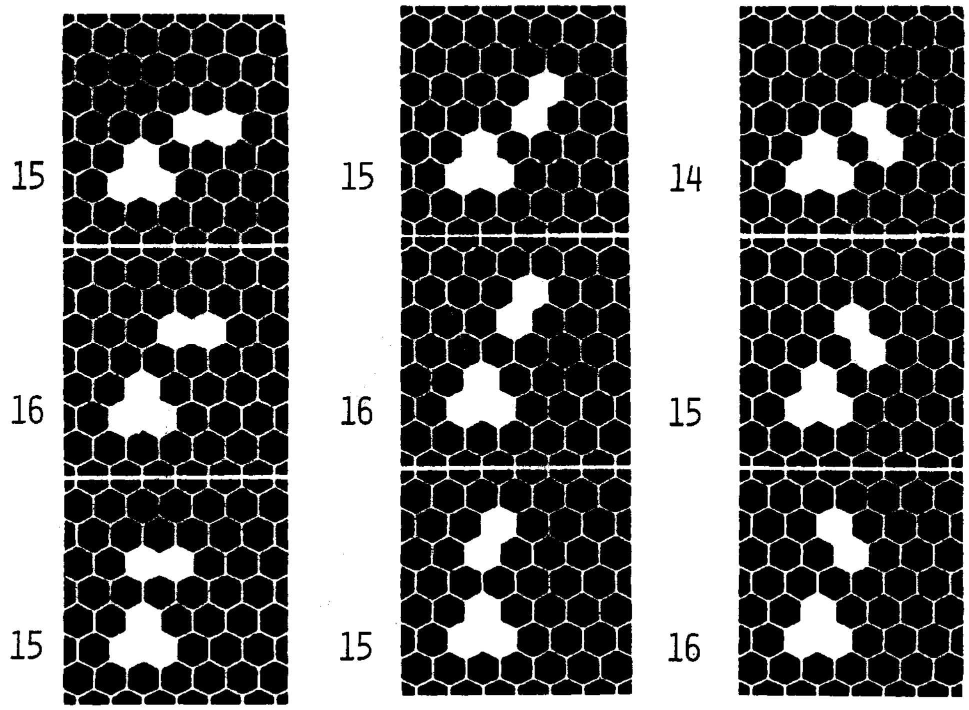


Figure 15. All constellations of one naphthalene and one phenalene hole which correspond to basic double coronoids. The values of $h = 9+8-x$ are given.

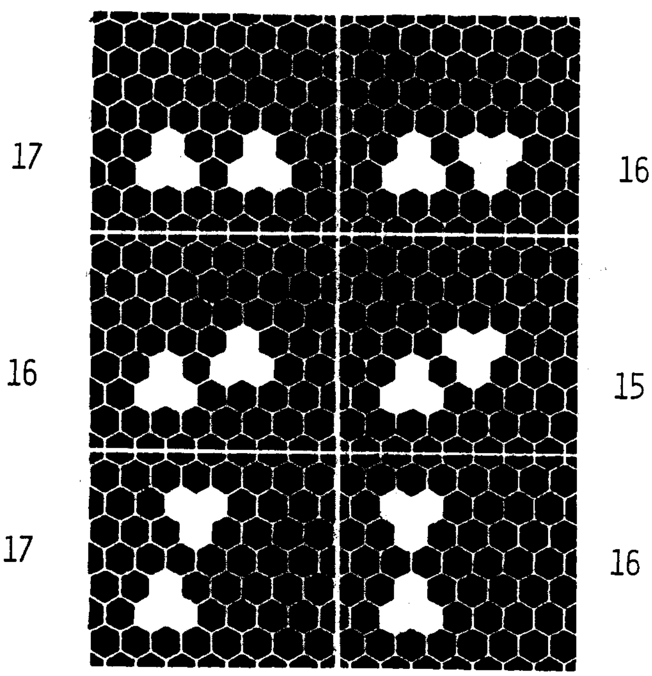


Figure 16. All constellations of two phenalene holes which correspond to basic double coronoids. The values of $h = 9+9-x$ are given.

numbers up to $h = 18$ were produced and are reported in Table VI (first column). In Table VII more detailed classifications are accounted for: the neo scheme, Δ values, and symmetry groups. It is noted that these systems (Table VII) exactly embrace all double coronoids with $h \leq 18$ and the particular constellation of two naphthalene holes as in the $h = 13$ double coronoid.

Tables VIII and IX were produced correspondingly by executing all possible additions of hexagons to the six systems with $h = 14$, and 15 systems with $h = 15$, respectively.

FORMS OF DOUBLE CORONOIDS

Systems with $h \leq 16$. The forms of all double coronoids up to $h = 15$ are depicted elsewhere.[43] Some of those with $h = 16$ are found in Figures 11–13 and 19.

Table VIII. Numbers of Double Coronoids Derived from the $h = 14$ Basic Systems

h	type[a]	Δ	D_{2h}	C_{2h}	C_{2v}	C_s	total
14	n	0	0	2	2	0	4
	o	1	0	0	0	2	2
15	n	0	0	0	2	30	32
	o	1	0	0	1	38	39
	o	2	0	0	0	7	7
16	n	0	0	16	14	307	337
	e	0	0	3	3	10	16
	o	1	0	0	1	425	426
	o	2	0	0	3	100	103
	o	3	0	0	0	9	9
17	n	0	0	0	23	2 650	2 673
	e	0	0	0	1	193	194
	o	1	0	0	7	3 745	3 752
	o	2	0	0	1	1 024	1 025
	o	3	0	0	1	109	110
	o	4	0	0	0	5	5
18	n	0	0	101	96	18 962	19 159
	e	0	0	22	16	2 195	2 233
	o	0	0	2	4	3	9
	o	1	0	0	9	28 615	28 624
	o	2	0	0	20	8 450	8 470
	o	3	0	0	2	1 071	1 073
	o	4	0	0	0	50	50
	o	5	0	0	0	1	1

[a] Abbreviations: see footnote a, Table V.

Figure 20 shows all the essentially disconnected double coronoids with $h = 16$. There are 26 such systems in accord with Table V. This table also accounts for all the $h = 16$ double coronoids with $\Delta = 3$. These 10 systems are depicted in Figure 21.

Concealed Non-Kekuléan Systems. The search for concealed non-Kekuléan polyhexes has been conducted with interest by several investigators for a long time.[51] It started with the consideration of benzenoids (polyhexes without holes) in general and continued with coronoids and different classes of benzenoids or coronoids. A concealed non-Kekuléan polyhex is, by definition, characterized by $\Delta = 0$ and $K = 0$. With

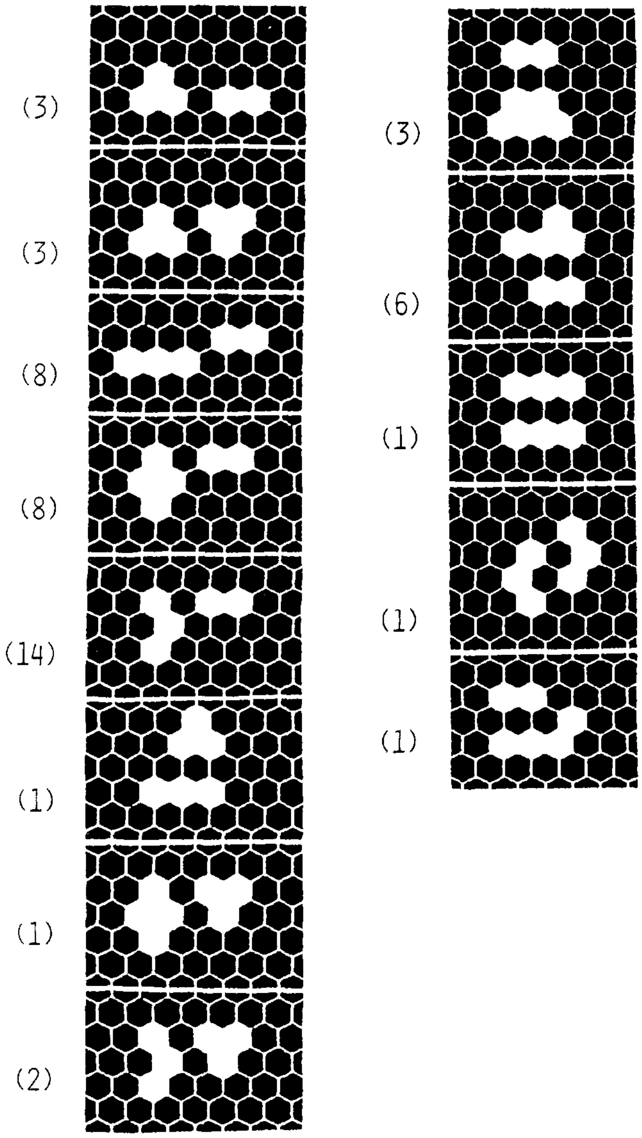


Figure 17. All pairs of holes which are encountered in $h = 16$ basic double coronoids. One constellation in each case is depicted; the numbers of constellations are indicated (in parentheses).

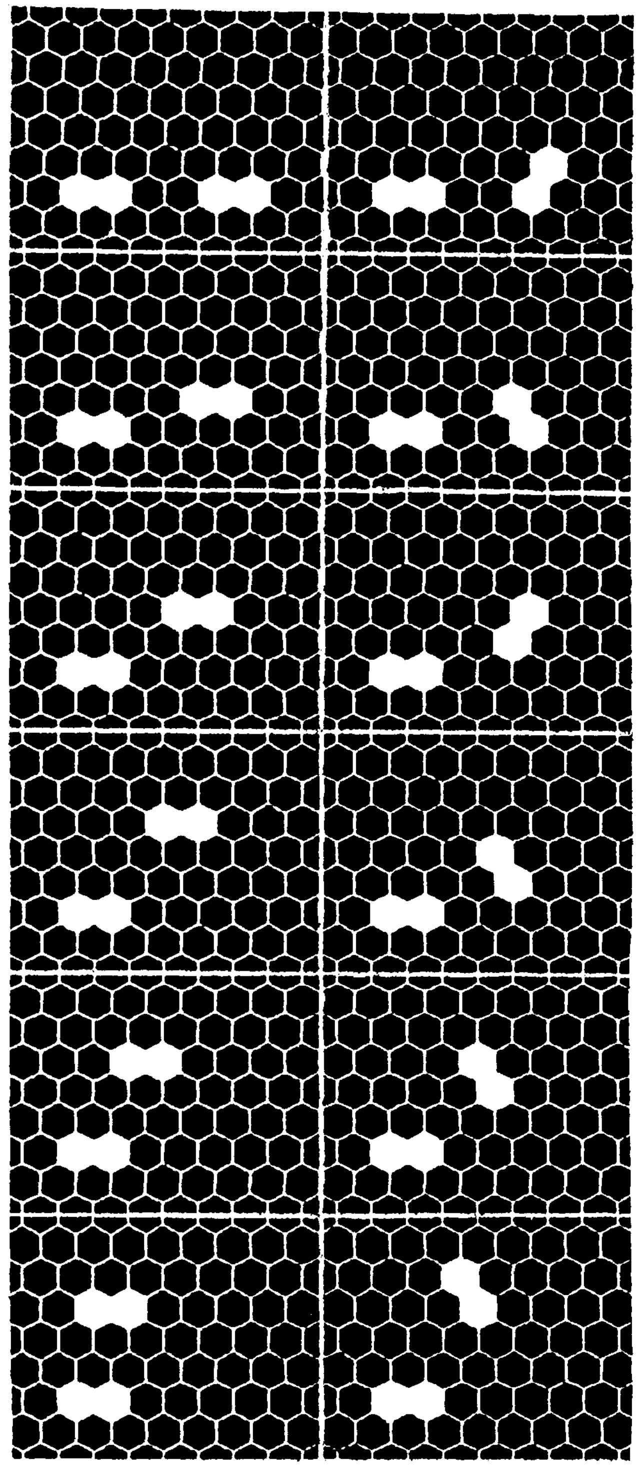


Figure 18. All constellations of holes for the nonbasic extra double coronoids with $h = 16$.

respect to the double coronoids, two examples of concealed non-Kekuléans with $h = 18$ as the smallest number of hexagons have been reported previously.[10] In the present computer-aided analysis we found in fact one smaller concealed non-Kekuléan double coronoid, viz., one with $h = 17$, and furthermore 11 such systems with $h = 18$. The forms are depicted in Figure 22. They were obtained from additions to the basic systems with $h = 13$ and $h = 14$, as is accounted for in Tables VII and VIII, respectively. A closer inspection revealed that these systems (Figure 22) are the only concealed non-Kekuléan double coronoids with the indicated numbers of hexagons.

KEKULÉ STRUCTURE COUNTS

Figures 11, 12, 19, and 20 are supplied with Kekulé structure counts (K numbers) for the pertinent (Kekuléan) double coronoid systems. These numbers were obtained from computer programs using the determinant of the adjacency matrix or, when necessary, the Pfaffian of a skew-symmetric adjacency matrix. The adaptation of these methods to coronoid systems is explained in some details elsewhere.[52] This kind of listing for K numbers of double coronoids is very useful as a support for analytical studies of these quantities. Very little work in this area has been done so far, as is described in the above introduction. In the following we show a few examples of analytical determinations of K numbers for some double coronoids.

The essentially disconnected systems are fairly manageable inasmuch as the total K number is obtained as the product of the Kekulé structure counts for effective units. Thus, for instance, the equal K numbers for the two last systems in Figure 20 are $K = 3 \times 416$, where 3 Kekulé structures pertain to naphthalene and 416 to the smallest ($h = 13$) double coronoid.[43,49] All the other systems in Figure 20 are more intricate. Here the effective units are degenerate (single) coronoids which possess edges not belonging to hexagons as parts of macrocycles. The phenomenon is exemplified in the following for the two systems with $K = 224$. They have only

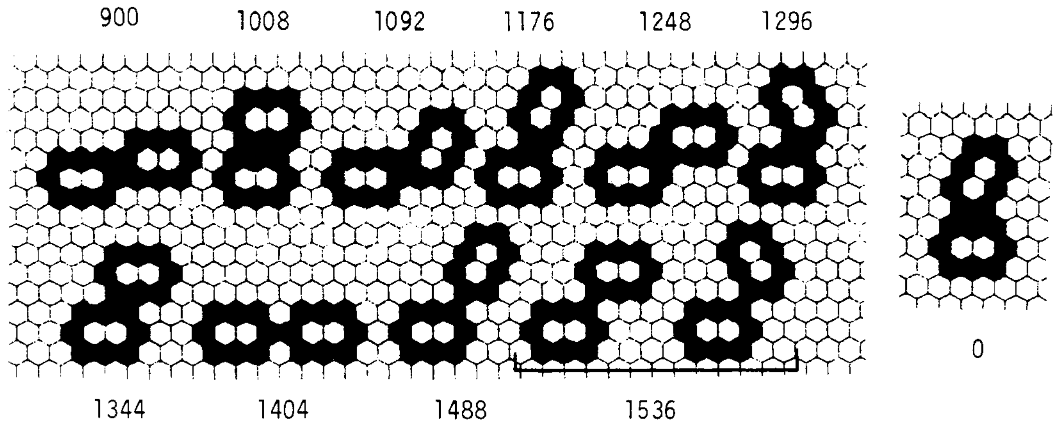


Figure 19. All nonbasic extra double coronoids for $h = 16$. K numbers are given. The Kekulêan ($K > 0$) systems have $\Delta = 0$; the non-Kekulêan ($K = 0$) has $\Delta = 1$.

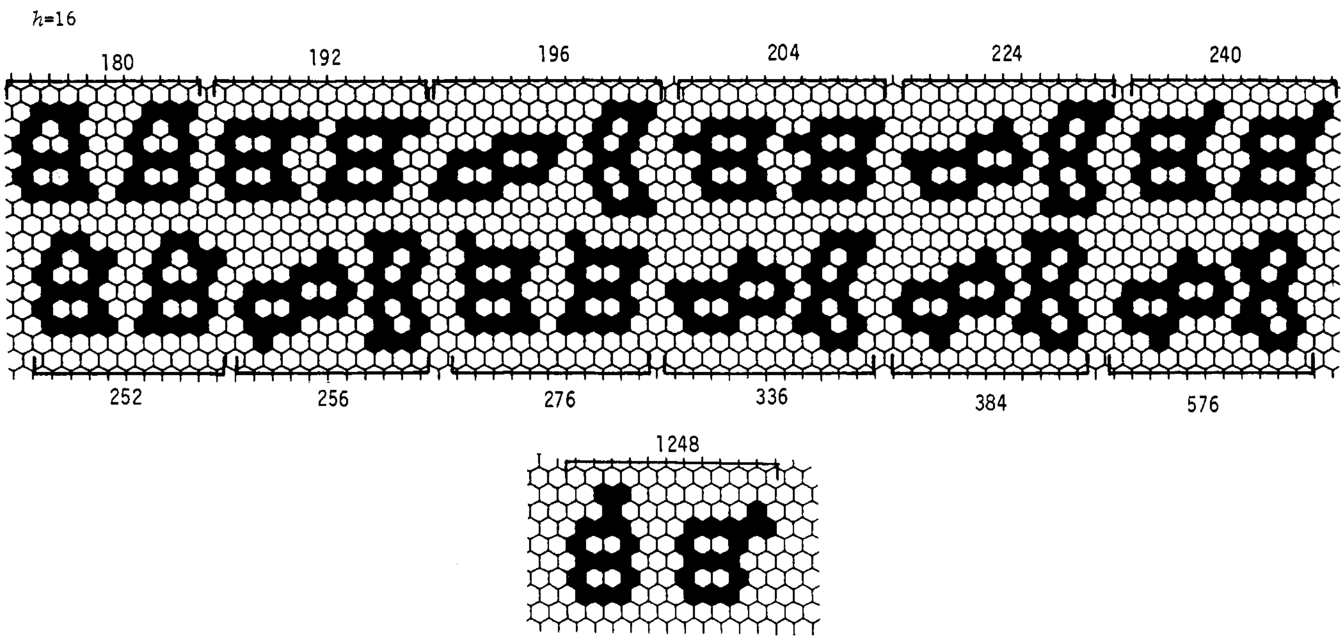


Figure 20. All essentially disconnected double coronoids for $h = 16$. K numbers are given.

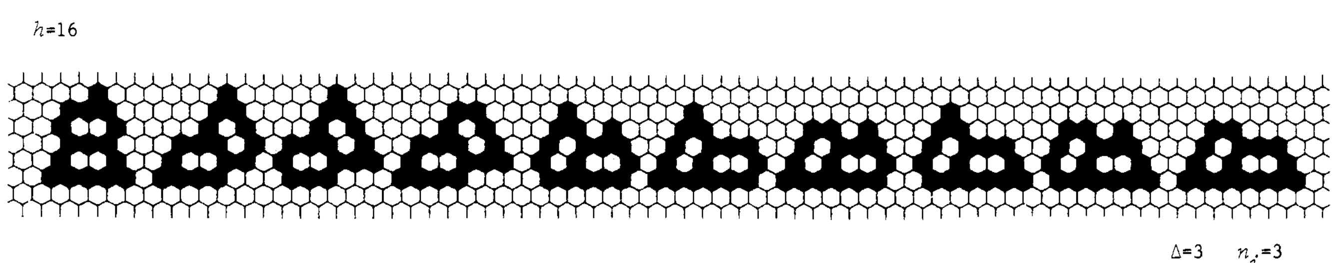


Figure 21. All (obvious non-Kekulêan) double coronoids with $\Delta = 3$.

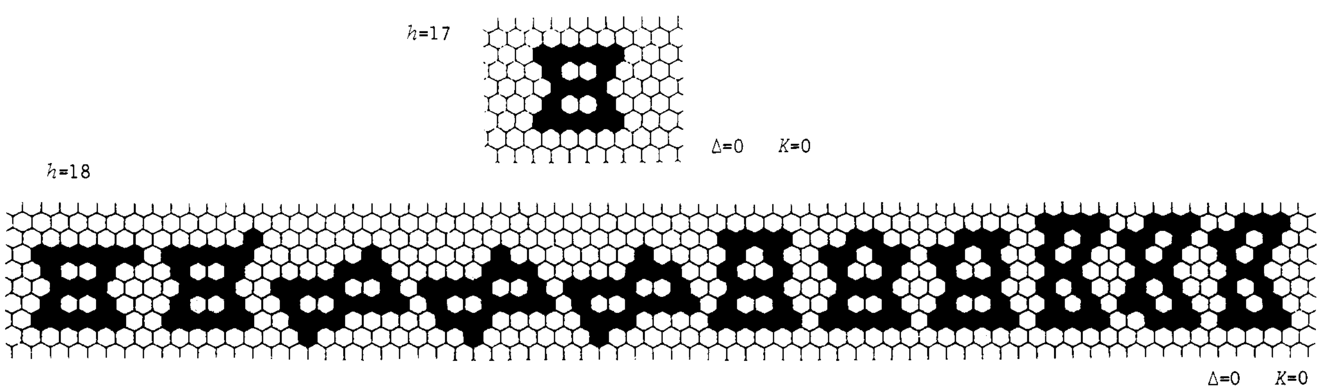


Figure 22. All concealed non-Kekulêan ($\Delta = 0$, $K = 0$) double coronoids with $h \leq 18$.

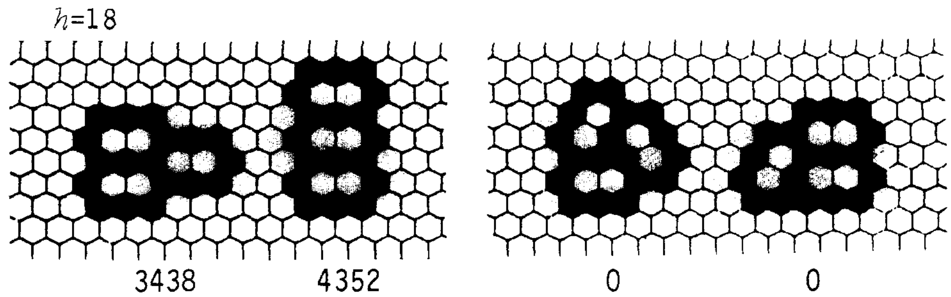
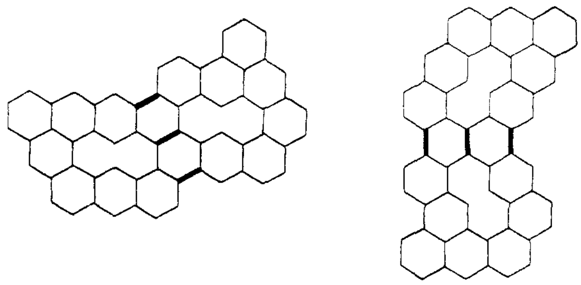
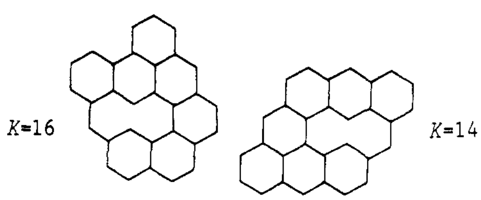


Figure 23. The four smallest (h = 18) triple coronoids. K numbers are given.

three fixed single bonds each, which are indicated with heavy lines.



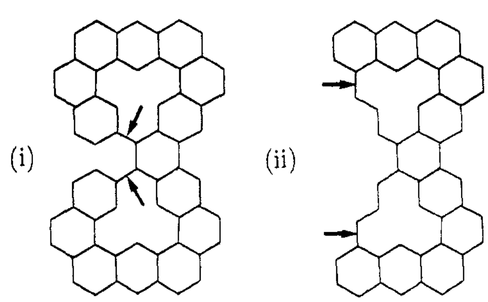
It turns out that the effective units are pairwise isomorphic. They are



The total K number is indeed equal to the product of the two numbers given on the above drawings.

The analysis of the Kekulé structure count for a normal double coronoid may be far more difficult. Take for example one of the primitive double coronoids of Figure 11, the one with K = 1188.

If the method of fragmentation[5,53] is applied to one of the vertical edges on the outer perimeter at the middle of the system, one obtains the two fragments:



The first fragment (i) may furthermore be split into

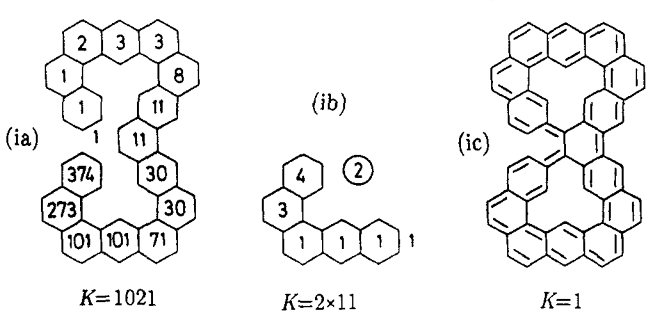
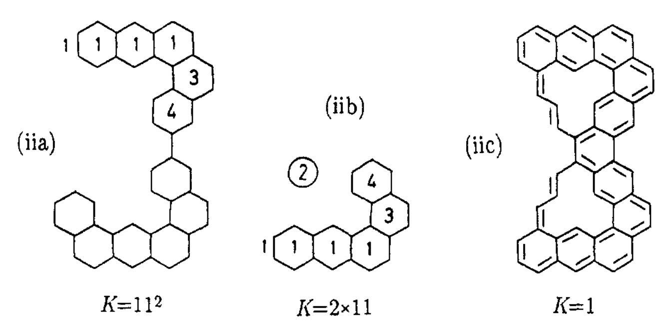


Table IX. Numbers of Double Coronoids Derived from the h = 15 Basic Systems

h	type[a]	Δ	D_{2h}	C_{2h}	C_{2v}	C_s	total
15	n	0	2	1	2	5	10
	o	1	0	0	0	5	5
	n	0	0	0	4	92	96
	o	1	0	0	4	118	122
	o	2	0	0	0	24	24
17	n	0	4	16	26	1 000	1 046
	e	0	0	2	2	18	22
	o	1	0	0	0	1 317	1 317
	o	2	0	0	11	385	396
	o	3	0	0	0	40	40
18	n	0	0	0	48	8 427	8 475
	e	0	0	0	3	384	387
	o	1	0	0	27	12 026	12 053
	o	2	0	0	0	3 906	3 906
	o	3	0	0	7	576	583
	o	4	0	0	0	27	27

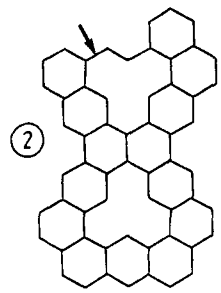
[a] Abbreviations: see footnote a, Table V.

This fragmentation was achieved by assuming the two bonds indicated by arrows in (i) to be single/single, double/single, and double/double, respectively. The structures with double/single and single/double bonds in the indicated positions are symmetrically equivalent; hence the multiplicity 2 for (ib), as is indicated by the encircled numeral. The Kekulé structure counts for the fragments (ia) and (ib), which are single benzenoid chains, are found as the sums of the indicated numbers according to the algorithm of Cyvin and Gutman,[5,54] which is a modification of the classical Gordon–Davison[55] algorithm. The third fragment has only one Kekulé structure, which is of the annulenoid type: the circumference is a conjugated circuit, while all the internal (radial) bonds are single. We have now for fragment (i): K(i) = 1021 + 2 × 11 + 1 = 1044. For fragment (ii), following the same procedure, we arrive at

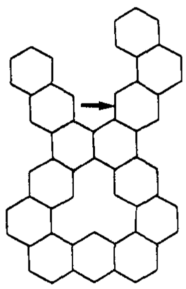
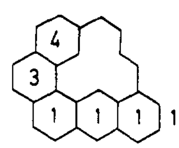


Therefore K(ii) = 144, and K(i) + K(ii) gives the total of 1188 Kekulé structure counts.

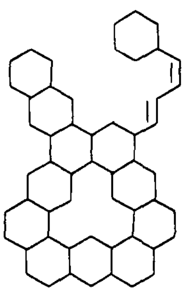
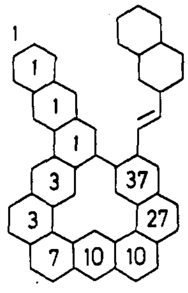
In another fragmentation scheme for the same system we can take advantage of symmetry from the start and consider, for instance, the two middle bonds at the top. They can be single/double or double/single, resulting in symmetrically equivalent fragments:



In the next step, on attacking the bond marked by an arrow, we arrive at

(i)  (ii) K=11+1 

Here fragment (i) may be split into

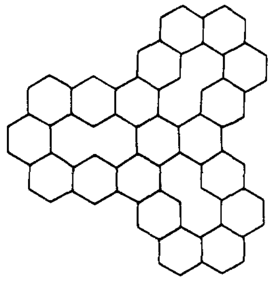
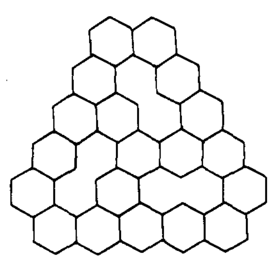
(ia)  (ib) 

K=2×138 K=3×(101+1)

The number 138 pertains to the Kekulē structure count for the naphtho-annelated cyclo[*d.e.e.d.e.e.d.e.e.*]nonakisbenzene. It can again be found by different fragmentation schemes. For the sake of brevity we shall not go into further details of this analysis but giving the net result, viz., $K = 2[K(\text{i}) + K(\text{ii})] = 2 \times (582 + 12) = 1188$.

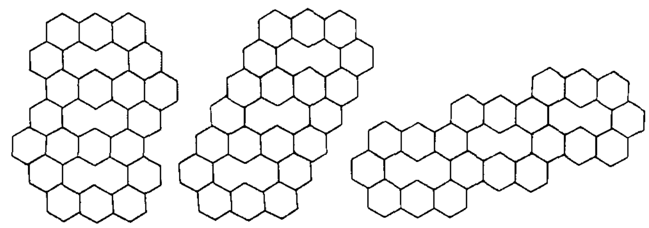
TRIPLE CORONOIDS

The four smallest triple coronoids, which have been identified and are mentioned in Survey of Enumerations, are depicted in Figure 23. The non-Kekulēan ($K = 0$) systems therein have $\Delta = 1$. The symmetries are C_{2v}, D_{2h}, C_{3h}, and C_s, respectively. It appears in other words that trigonal symmetry is possible, in contrast to the situation for double coronoids. Also D_{3h} systems are found, as is demonstrated by

K=6169 K=0

The diagram shows two triple coronoids with $h = 19$, a Kekulēan system (left), and a non-Kekulēan (right). The latter system is the smallest triple coronoid with $\Delta = 3$. Finally also the C_{2h} symmetry is represented, but not for smaller systems than those with 20 hexagons. Below we show three examples.



K=5924 K=736 K=7504

These are three representatives of the nine Kekulēan triple coronoids with C_{2h} symmetry that we have identified. The hexagonal symmetries (D_{6h} or C_{6h}) are not possible for triple coronoids.

CONCLUSION

The present work deals mainly with the enumeration and anatomy of double coronoids, for which the interest is clearly growing among the mathematical chemists. There is obviously much more to be done in this area. Firstly, the extension to larger systems would not only be a routine production of larger numbers. New features are expected to be encountered under way, and some work in this direction is already in progress.

ACKNOWLEDGMENT

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Global Energy Minimization by Rotational Energy Embedding

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Given a sufficiently good empirical potential function for the internal energy of molecules, prediction of the preferred conformations is nearly impossible for large molecules because of the enormous number of local energy minima. Energy embedding has been a promising method for locating extremely good local minima, if not always the global minimum. The algorithm starts by locating a very good local minimum when the molecule is in a high-dimensional Euclidean space, and then it gradually projects down to three dimensions while allowing the molecule to relax its energy throughout the process. Now we present a variation on the method, called rotational energy embedding, where the descent into three dimensions is carried out by a sequence of internal rotations that are the multidimensional generalization of varying torsion angles in three dimensions. The new method avoids certain kinds of difficulties experienced by ordinary energy embedding and enables us to locate conformations very near the native for avian pancreatic polypeptide and apamin, given only their amino acid sequences and a suitable potential function.

INTRODUCTION

The fundamental problem in the conformational analysis of large molecules is that the conformers of physical interest correspond to the best few local energy minima out of a total number of minima that apparently increases exponentially with the size of the molecule. An increasingly popular approach is to rely on large but insufficient amounts of experimental data to restrict the geometric possibilities so much that sampling experimentally allowed conformations by distance geometry embedding or simulated annealing produces structures relatively near the correct state(s). Then energy refinement by constrained molecular dynamics can produce a relatively small number of low energy conformers satisfying all the experimental constraints. For a sampling of recent activity along these lines, see the references.[1-9] On the other hand, suppose we have very little experimental information beyond standard bond lengths, bond angles, and van der Waals radii. Then we are forced to rely almost exclusively on some given energy function to guide the search for the best conformations. If we treat the calculation of internal energy as a black box, where we put atomic coordinates in and we get an energy value and its gradient out, then global optimization methods hold little hope for finding global and nearly global energy minima without spending an exponentially increasing amount of computer time for larger and larger molecules.[10] One approach to escaping from this difficulty is to build into the global search procedure more a priori knowledge about the energy function. Our particular efforts along this line have concentrated on exploiting the large geometric component to the problem, which is made clearest when the energy function, E, is some sort of classical molecular mechanics potential. Such energies are calculated largely as a sum of atom-atom pairwise interactions, where the n atoms are treated as points engaged in isotropic interactions, and for each term there is often a unique, finite, optimal separation. Although we are of course interested in simulating molecules in ordinary three-dimensional space, $\mathcal{R}^3$, the *energy embedding* algorithm[11-14] first locates a good local minimum in $\mathcal{R}^{n-1}$, where there are few

