Molecular Vibrations of Cyclo[d.e.e.d.e.e.d.e.e]nonakisbenzene and the Topology of Primitive Coronoids with Trigonal Symmetry

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Cyclo[d.e.e.d.e.e.d.e.e]nonakisbenzene, $C_{36}H_{18}$ (C_1), is a polycyclic aromatic hydrocarbon belonging to the cycloarenes. It corresponds to the graph-theoretically defined systems of hexagons called primitive coronoids and has trigonal symmetry.

A simple Hückel molecular orbital analysis was performed for C_1.

The molecular vibrations of C_1 were analyzed. A previously developed force field for condensed aromatics was used to calculate the vibrational frequencies. Mean amplitudes of vibration for selected interatomic distances are reported.

Primitive coronoids of trigonal symmetries (D_{3h} and C_{3h}) were enumerated by computer aid up to $h = 30$ for C_{3h} and up to $h = 66$ for D_{3h}. Here, h is used to denote the number of hexagons. The actual forms are depicted up to $h = 21$ for C_{3h} and up to $h = 24$ for D_{3h}.

The numbers of Kekulé structures (K) for primitive coronoids with trigonal symmetry were treated. A general combinatorial K formula for these systems was derived by means of the symmetry-adapted method of fragmentation.

Dedicated to Professor Otto Bastiansen on his 70th birthday

The cycloarenes constitute a new class of polycyclic aromatic hydrocarbons. The chemistry of these systems is comprehensibly surveyed in a series of five papers.[1–5] Coronoids[6] (which are synonymous with true circulenes[7]) are defined mathematically (or graph-theoretically) in the theory of molecular topology, and have obvious counterparts in cycloarenes. The definition of coronoids is closely connected with that of benzoids.[8,9]

A benzenoid is a planar system of simply connected identical regular hexagons. The system may be taken out of a hexagonal lattice by defining a cycle of edges, which is called the perimeter. The perimeter corresponds to the carbon skeleton of an annulene.

A coronoid (or corona-condensed[10] benzenoid) is (like a benzenoid) a planar system of identical regular hexagons, but has a hole (here referred to as the corona hole) defined by an inner perimeter completely embraced by the outer perimeter. The corona hole should have a size of at least two hexagons.

A primitive coronoid is characterized by a single chain of hexagons in a circular arrangement. These hexagons may be linearly (L) or angularly (A) annelated, giving rise to the LA-sequence.[11] This sequence is reflected in the currently applied nomenclature[1] for the cycloarenes in organic chemistry, as also used in the present title. The title compound, for instance, corresponds to a primitive coronoid with the LA-sequence LAALAALAA. It should be noted that the concept of cycloarenes is somewhat more general than that of primitive coronoids. Thus, for instance, cyclo[d.e.d.e.d.e.d.e.d.e]decakisbenzene, which has been attempted synthesized,[4] cannot be con-

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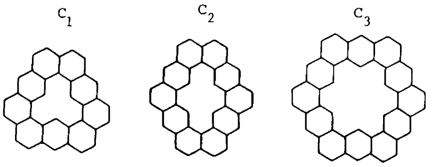

Fig. 1. Three primitive coronoids or cycloarenes: $C_{36}H_{18}$ (C_1), $C_{40}H_{20}$ (C_2) and $C_{48}H_{24}$ (C_3).

structed as a planar system of regular hexagons and has therefore no counterpart among coronoids.

Fig. 1 shows three cycloarenes, which all correspond to primitive coronoids (C_1, C_2 and C_3). They consist of 9, 10 and 12 hexagons, and have the symmetries D_{3h}, D_{2h} and D_{6h}, respectively. The corresponding hydrocarbons are: cyclo[d.e.e.d.e.e.d.e.e]nonakisbenzene (the title compound, C_1), cyclo[d.e.d.e.e.d.e.d.e.e]decakisbenzene (C_2), and cyclo[d.e.d.e.d.e.d.e.d.e.d.e]dodecakisbenzene or kekulene (C_3).

The route to the synthesis of a cycloarene has been long and troublesome[12,13] (see also the review[1]). Actually, the first report on attempts to synthesize C_3 (Fig. 1) was given in 1965 by H. A. Staab at the Annual Meeting of *Gesellschaft Deutscher Chemiker* in Bonn (Kekulé centennial). At this meeting the C_3 molecule was named kekulene. Not until 13 years later[14] was the first successful synthesis of kekulene reported. A further 8 years later[5] the second cycloarene, viz. C_2, was synthesized. The prospects of synthesizing also the cycloarene C_1 of Fig. 1 are now very good,[4] as was also communicated privately by H. A. Staab to one of the present authors (S.J.C.).

The first part of the present paper deals with a normal coordinate analysis of the molecular vibrations of C_1 (Fig. 1). Calculated vibrational frequencies for a cycloarene are given for the first time. Mean amplitudes of vibration[15] are also reported.

The next part of this paper concerns molecular topology. Primitive coronoids with trigonal symmetry are enumerated by computer aid, and the numbers of Kekulé structures (K)[16] of such systems are treated. A general solution is presented.

Some results of computer-aided enumerations and classifications for coronoids have been reported,[6,17–20] but still much work in this area remains to be done. Also, a few papers containing K formulas for special coronoids are available,[19,21–28] but far fewer than those with K formulas for benzenoids.[13]

Cyclo[d.e.e.d.e.e.d.e.e]nonakisbenzene (C_1)

Molecular model. A planar trigonal (symmetry D_{3h}) molecular model of C_1 was assumed. We are well aware of the fact that this is only a first approximation and that some deformation would be more realistic, in accordance with the theoretical work by Vogler.[29] It seems at least quite certain that the three hydrogens inside the corona hole are twisted out of the plane. Furthermore, we assume all the benzenoid rings to be regular and identical, and all valence angles (CCH as well as CCC) to be 120°. This idealized model is determined by two structural parameters, which were estimated to be 140 pm and 110 pm for the CC and CH bonds, respectively.

Hückel molecular orbital analysis. The simple Hückel molecular orbital analysis was performed

Table 1. Energy levels as $\pm x$ according to the simple Hückel molecular orbital theory for cyclo[d.e.e.d.e.e.d.e.e]nonakisbenzene.

Species (D_{3h})	$\lvert x\rvert$		
a_1'	1.618	0.618	
a_2''	2.621	1.659	1.512
e''	2.451	2.047	1.451
	1.161	1.000	0.591

Table 2. Bond orders (P), theoretical bond distances (R) and force constants (f) for CC bonds in cyclo[d.e.e.d.e.e.d.e.e]nonakisbenzene.

CC bond	P	R/pm	f/Nm^{-1}
a	0.766	138.0	522
b	0.514	142.5	434
c	0.509	142.5	433
d	0.502	142.7	430
e	0.610	140.7	466
f	0.480	143.1	423
g	0.615	140.6	468
h	0.585	141.2	458

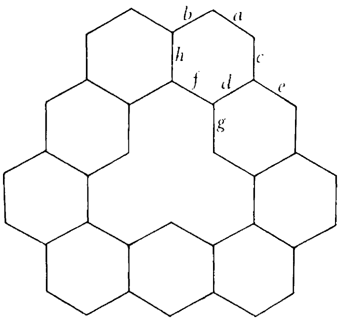

Fig. 2. Identification of the CC bonds in C_1.

in the symmetrized form according to the symmetrical structure for the π-system:

$$\Gamma_\pi = 4a_1'' + 8a_2'' + 12e'' \qquad (1)$$

The π-energy levels in β units (conventionally denoted by x, which is dimensionless) are summarized in Table 1. Not only the energy levels (eigenvalues) were computed, but also the coefficients of molecular orbitals (eigenvectors). They were used to calculate Coulson bond orders (P) for the eight types of CC bond distances (cf. Table 2 and Fig. 2). By means of the empirical formula[30]

$$r/\text{pm} = 153.6 - 19.2P/[100P + 76.5(1-P)] \qquad (2)$$

the (theoretical) bond distances were obtained as shown in Table 2. The weighted average of these bond distances is 141.4 pm. The value is close enough to the approximate estimate (140 pm) used in the subsequent vibrational analysis, since the precision of structural parameters is not critical for this purpose. Some investigations to this effect have been made specifically for the polycyclic aromatic hydrocarbon coronene.[31]

Force field. A simple force field established for polycyclic aromatic hydrocarbons and referred to as the five-parameter approximation[32-35] was employed. It actually contains five parameters for in-plane and five parameters for out-of-plane vibrations. Refined force constants for the CC stretchings (counted as one parameter) were computed from the bond orders (P) according to an adaptation of Badger's rule to polycyclic aromatic hydrocarbons[36] (eqn. 3).

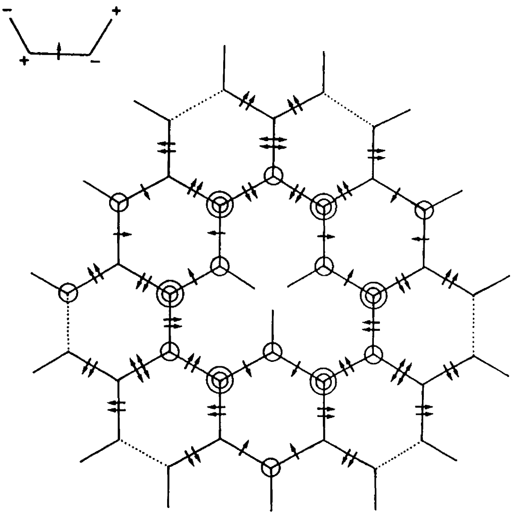

Fig. 3. Symbolically indicated out-of-plane valence coordinates used to generate a complete set of independent e'' symmetry coordinates. The auxiliary figure (top left) shows the indication of a "boat" torsion. Circles indicate out-of-plane bendings.

$$f/\text{Nm}^{-1} = 179.3[(23.5P + 76.5)/(0.916P + 654.8)]^3 \qquad (3)$$

The numerical values are included in Table 2. The other force-constant parameters are (in Nm^{-1}): 500 for the CH stretchings, 40 for the CCC bendings where the central C atom is bonded to another C, 70 for the CCC bendings where the central C atom is bonded to an H, 35 for the CCH bendings, 15 for the CCCC out-of-plane bendings, 20 for the CCCH out-of-plane bendings, 5 for all "boat" torsions, i.e. the CCCC, CCCH and HCCH types, 2 for the CCCC/CCCC torsion/torsion interactions pertaining to the same CC bond, and, finally, 7 for the corresponding torsion/torsion interactions of the types CCCC/CCCH and CCCC/HCCH.

Symmetry coordinates. The vibrational analysis was symmetrized in the usual way by producing symmetry-adapted linear combinations of valence coordinates. The symmetrical structure (distribution of the normal modes of vibration into the symmetry species of the D_{3h} group) is:

$$\Gamma_{\text{vib}} = 18a_1' + 17a_2' + 35e' + 6a_1'' + 11a_2'' + 17e'' \qquad (4)$$

Here, we do not give all details of the construction of the symmetry coordinates. The main problem was to eliminate redundancies so as to end up with a complete set of independent coordinates. Here, the out-of-plane coordinates belonging to the *e''* species presented the most difficult part of the problem. For this particular case we indicate (see Fig. 3) the boat torsions (arrows) and out-of-plane bendings (circles around the central atom). Double arrows and double circles indicate that two different linear combinations of the same set were used. The bonds indicated by dotted lines in Fig. 3 are not involved in any of the valence coordinates (neither in-plane or out-of-plane) which were used to construct the symmetry coordinates.

Vibrational frequencies. The above-outlined methods resulted in the calculated vibrational frequencies given in Table 3. The spectroscopic activities are also indicated in the table. In conclusion, we predict 35 fundamentals active in Raman only, 11 in infrared only, and 35 both Raman and infrared active. Also, the orders of magnitude should be compatible with those of Table 3.

Mean amplitudes of vibration. The simple force-field approximation employed here has been

Table 3. Calculated vibrational frequencies (cm^{-1}) for cyclo[d.e.e.d.e.e.d.e.e]nonakisbenzene.[a] The species designations pertain to the D_{3h} group.

Species a_1'	3038	Species e'	3038	Species a_1''	957
(Ra,p)	3035	(IR + Ra,dp)	3037	(ia)	825
	3034		3034		696
	3032		3034		478
	1613		3032		354
	1576		3031		132
	1481		1677		
	1446		1643	Species a_2''	982
	1355		1583	(IR)	959
	1245		1556		922
	1121		1532		979
	1059		1517		848
	902		1487		654
	758		1426		531
	662		1423		417
	478		1390		350
	396		1304		162
	257		1243		78
			1182		
Species a_2'	3037		1158	Species e''	974
(ia)	3032		1129	(Ra,dp)	961
	1672		1070		940
	1597		1031		919
	1562		1014		894
	1472		970		852
	1443		904		822
	1310		758		761
	1221		693		588
	1150		659		550
	1097		560		492
	1026		544		431
	846		502		318
	750		389		279
	534		249		229
	482		177		154
	335				62

[a] Abbreviations: d depolarized; ia inactive; IR infrared-active; p polarized; Ra Raman active.

Table 4. Calculated mean amplitudes of vibration (pm) for selected interatomic distances in cyclo[d.e.e.d.e.e.d.e.e]nonakisbenzene. Parenthesized values (*R*) are the equilibrium distances (pm).

Atoms	*i–j*	(*R*)	*T* = 0	298 K
CC	1–2	(140)	4.69	4.80
	1–3	(242)	5.61	6.11
	1–4	(370)	5.67	6.26
	1–5	(485)	5.93	6.91
	1–6	(505)	6.30	7.81
	1–7	(420)	6.49	7.99
	2–3	(140)	4.67	4.74
	2–6	(420)	6.17	7.41
	2–7	(370)	6.55	8.08
	2–8	(485)	6.47	8.21
	2–11	(280)	6.24	7.36
	2–12	(242)	5.52	6.00
	3–11	242	6.62	8.01
	1–13	(700)	6.53	8.12
	2–13	(642)	6.54	8.07
	3–13	(505)	6.62	8.00
	25–13	(840)	6.66	8.33
	26–13	(918)	6.81	8.45
	27–13	(874)	6.86	8.53
CH	1–3′	(266)	12.49	12.96
	2–3′	(217)	9.98	10.04
	3–3′	(110)	7.74	7.74
	6–3′	(244)	13.37	14.39
	7–3′	(157)	12.22	13.36
	8–3′	(269)	10.67	11.87
	9–3′	(310)	9.72	10.80
	1–13′	(810)	9.75	10.89
	25–13′	(950)	9.84	11.05
	26–13′	(1027)	10.00	11.19
HH	3′–7′	(52)	13.93	14.97
	3′–18′	(642)	12.53	13.51
	3′–19′	(608)	13.99	15.13
	3′–21′	(546)	14.56	15.62
	3′–23′	(586)	15.69	16.67
	3′–24′	(603)	15.16	15.79
	3′–26′	(593)	14.01	14.37
	3′–27′	(557)	13.11	13.30
	3′–29′	(500)	11.83	11.96

used to calculate mean amplitudes of vibration[15] several times[32,37–39] (see also other parts of the series "Condensed Aromatics" as cited in Ref. 35). Some of these papers include systematic compilations of mean amplitude values for different types of interatomic distances.[39,40].

The mean amplitudes of vibration at absolute zero and 298 K were computed for all types of interatomic distances (bonded and non-bonded) in the molecule under consideration. The resulting material is far too voluminous to be reproduced here. Furthermore, the data did not provide any surprises when compared with the characteristic values for corresponding distance types from other condensed aromatics. We therefore give results for only a selection of interatomic distances, all of them being connected with the corona hole and therefore containing new types (see Table 4 and Fig. 4).

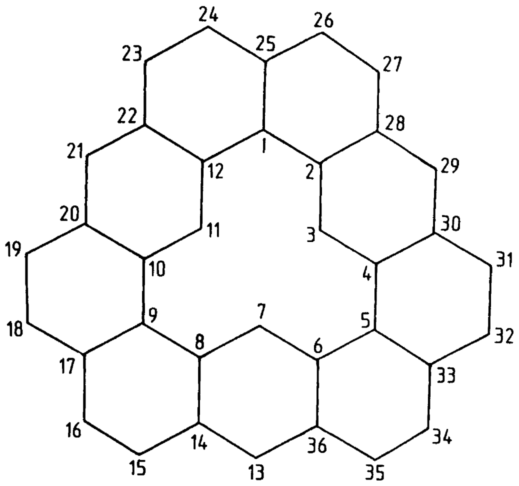

Fig. 4. Numbering of atoms in C_1. Hydrogen atoms are identified by primed numbers: 3′ directly bonded to 3, 7′ to 7, etc.

The first part of Table 4 lists all the CC distance types for the atoms on the inner perimeter, two bonded and eleven non-bonded; for the applied numbering of the atoms, see Fig. 4. The next six entries concern additional non-bonded CC distances, all of them crossing the corona hole, but the list is not complete. The subsequent group (CH distances) account for all types within the corona hole, one bonded and six non-bonded. For the rest of the CH distances, again only a selected number of types are included. With regard to the HH distances we have included all the types which involve one or two H atoms inside the corona hole.

General remarks. By the development of the method applied to the C_1 molecule above, the analysis of molecular vibrations for a polycyclic aromatic hydrocarbon has been reduced to a topological problem. Not a single piece of experimental data was invoked (and is not available at present) for the particular molecule C_1 in order to deduce the results. In mathematical terms one may say that the benzenoid/coronoid graph determines the vibrational problem. The available results include the force field and consequently the vibrational frequencies and molecular parameters like the mean amplitudes. The analysis of the simple Hückel molecular orbitals is another well-known topological problem,[41] in which the parameters (α, β) usually are kept "anonymous", i.e. without numerical values assigned to them. In the present case of the vibrational problem it must be admitted that a number of empirical parameters with numerical values are invoked.

Primitive coronoids with trigonal symmetry

Introductory remarks and definitions. A primitive coronoid[6] (see also the present introduction) consists of a number of segments which is equal to the number of A (angularly annelated) hexagons. A segment is defined as a linear chain of hexagons between, and including, two neighbouring A hexagons. In other words, an A hexagon belongs always to two (neighbouring) segments.

The A hexagons of a primitive coronoid are also called corners. A corner may be protruding or intruding. A protruding corner has three edges on the outer perimeter, while an intruding one has three edges on the inner perimeter.

In a primitive coronoid the total number of segments (or corners), S, is invariably an even number.

A primitive coronoid has at least six segments. If it has exactly six segments, it is called a hollow hexagon.[6] In a hollow hexagon all the (six) corners are protruding. All three systems in Fig. 1 are hollow hexagons.

Primitive coronoids with $h \leq 20$ amount to 10536 systems.[20] Among these systems there are only 16 with trigonal symmetry (D_{3h} or C_{3h}). The enumeration of the numbers of this class of primitive coronoids is one of the subjects of the present work. It is clear that this task cannot be solved efficiently by considering the primitive coronoids with trigonal symmetry only as a subclass of all primitive coronoids. However, fortunately we found a method for generating and enumerating the systems of interest specifically.

As for the benzenoids with trigonal symmetry,[42] we distinguish between primitive coronoids with trigonal symmetry of the first kind and of the second kind:

(i) a primitive coronoid with trigonal symmetry of the first kind has a hexagon in the center of its corona hole (or the corresponding benzenoid),
(ii) a primitive coronoid with trigonal symmetry of the second kind has a vertex in the center of its corona hole (or the corresponding benzenoid).

According to our approach these two kinds were generated separately.

Finally, in this section some general remarks on the number of Kekulé structures (K) are warranted. The K number of a primitive coronoid is completely determined by the LA-sequence of the system. Two systems with the same LA-sequence (and therefore the same K number) are said to be isoarithmic.[43] Two isoarithmic primitive coronoids have also the same sequence of segments. This sequence is specified in terms of the numbers of hexagons of each segment as, for instance, /3, 2, 3, 2, 3, 2/ for C_1 of Fig. 1. In an abbreviated notation: /3, $2/^3$. Correspondingly, for the system C_2 one may write /3, 3, $2/^2$ or /3^2,$2/^2$, and finally for the system C_3, $/3/^6$.

It is noted that two primitive coronoids, with the same or different numbers of hexagons, may possess the same K number "accidentally" without being isoarithmic.

Generation and enumeration. This is not the place to describe in detail the computerized procedure for the successive generation of all non-isomorphic primitive coronoids of trigonal symmetry with given (increasing) values of h. The main computer program for benzenoids has been described elsewhere,[44] as well as its adaptation to coronoids.[6] Furthermore, specific generation of benzenoids with hexagonal symmetry,[45] as well as coronoids with hexagonal symmetry[19] has been reported. A corresponding analysis has also recently been performed for benzenoids of trigonal symmetry.[46] In the present case of coronoids, as well as for the benzenoids,[46] the systems with trigonal symmetry of the first (i) and second (ii) kind were generated separately.

Table 5 shows the derived numbers of primitive

Table 5. Numbers of primitive coronoids with trigonal symmetry (D_{3h} and C_{3h}); $h \leq 30$.

h	Kind	D_{3h}	C_{3h}	Total
9	(ii)	1	0	1
12	(i)	1	0	2
	(ii)	1	0	
15	(i)	1	0	4
	(ii)	1	2	
18	(i)	3	1	9
	(ii)	2	3	
21	(i)	1	4	20
	(ii)	4	11	
24	(i)	11	10	51
	(ii)	6	24	
27	(i)	5	30	117
	(ii)	8	74	
30	(i)	29	84	302
	(ii)	15	174	

Table 6. Numbers of primitive coronoids with regular trigonal symmetry (D_{3h}); $33 \leq h \leq 66$.

h	Kind	D_{3h}	h	Kind	D_{3h}
33	(i)	10	51	(i)	229
	(ii)	25		(ii)	429
36	(i)	85	54	(i)	1735
	(ii)	42		(ii)	773
39	(i)	33	57	(i)	572
	(ii)	59		(ii)	1206
42	(i)	232	60	(i)	4717
	(ii)	107		(ii)	2122
45	(i)	77	63	(i)	1641
	(ii)	169		(ii)	3164
48	(i)	635	66	(i)	?
	(ii)	294		(ii)	5678

coronoids of symmetries D_{3h} and C_{3h} for h values up to 30. The actual forms up to $h = 21$ are displayed in Fig. 5.

The analysis for the D_{3h} systems specifically was carried out through $h = 66$. The results are found in Table 6. Fig. 6 shows the forms of all these systems for $h = 24$.

Numbers of Kekulé structures. The standard method of fragmentation for determination of the number of Kekulé structures (K) is due to Randić.[47] A useful modification of this method has been proposed under the name symmetry-adapted method of fragmentation[19, 25–28, 42, 46] In the present work we employ a special variant of the symmetry-adapted method of fragmentation[46] for the primitive coronoids of trigonal symmetry. In preparation, a description of some topological properties of such systems is warranted. The different statements are given here without proof.

The number of hexagons (h) of a primitive coronoid of trigonal symmetry is

$$h = 3\xi; \ \xi = 3, 4, 5, \cdots \tag{5}$$

Systems of the second kind are found for all the allowed h values, and those of the first kind for all $h \geq 12$ (cf. Tables 5 and 6). The deductions in the following apply to the coronoids of both kinds.

In a primitive coronoid of trigonal symmetry there are always at least two sets of three protruding corners each, which are symmetrically equivalent with respect to the rotation of 120°. Select two symmetrically equivalent corners, both either protruding or intruding. In between two such corners there must necessarily occur an odd number of corners, of which the intruding corners, if any, are even in number.

Define a single unbranched chain of hexagons, U, as a unit of a primitive coronoid between two symmetrically equivalent corners with respect to the rotation of 120°. Both these corners are included in U. According to the topological properties stated above, the number of segments in U, say s, must be even. The total number of segments is

$$S = 3s \tag{6}$$

When it is realized that S always is even, one may in fact perceive directly from (6) that also s must be even.

We are now in a position to demonstrate the application of the special variant[46] of the symmetry-adapted method of fragmentation to the coronoid C_1 of Fig. 1. Select three free edges (i.e. edges between two vertices of the second degree)

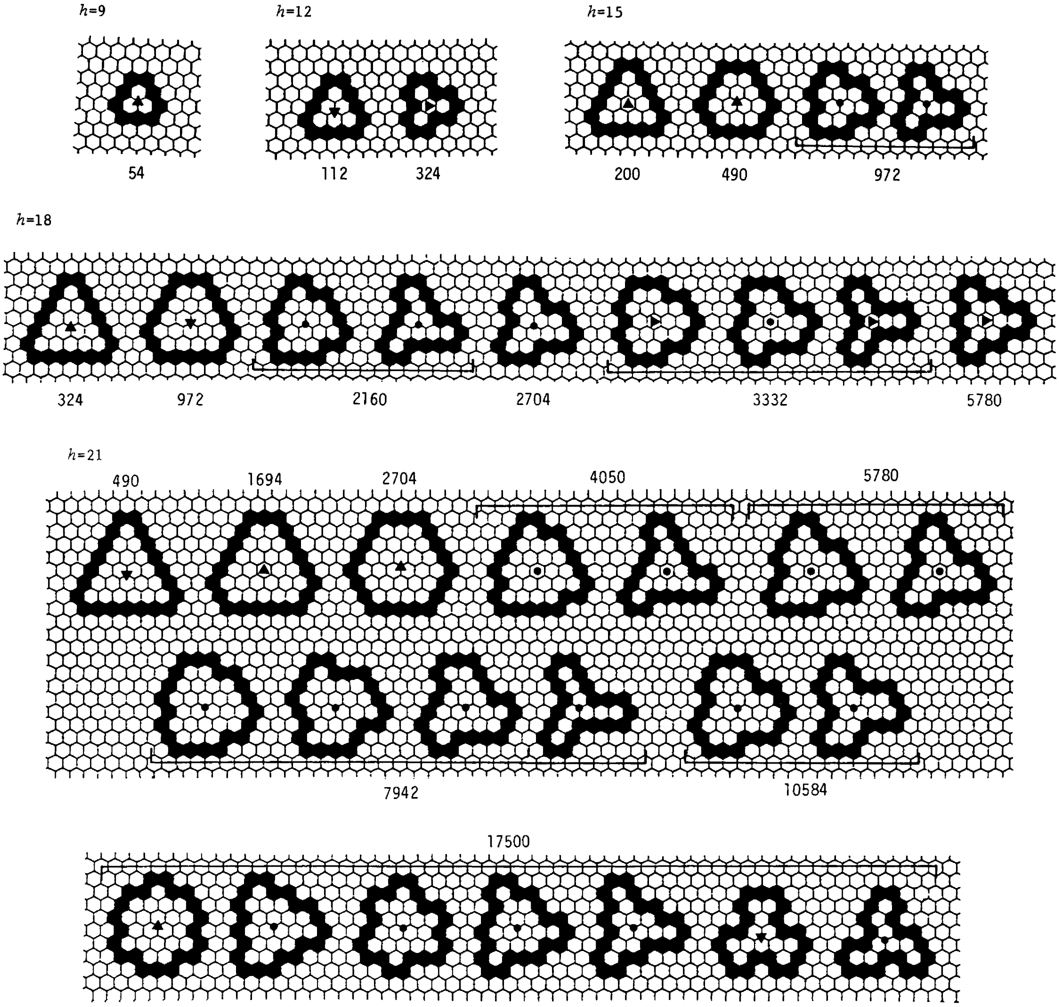

Fig. 5. All primitive coronoids of trigonal symmetry for $h \leq 21$. ▲ symmetry D_{3h}; ● symmetry C_{3h}. The first (i) or second (ii) kind is recognized by the position of the appropriate symbol in the centre of the corona hole. K numbers are given. Bracketed systems are isoarithmic.

of symmetrically equivalent corners. Assume the four possible bonding schemes for these edges as shown in Fig. 7: (1) all three single, (2) all three double, (3) two single and one double, and finally (4) one single and two double. Fig. 7 includes the multiplicities,, i.e. the numbers of (symmetrically equivalent) ways in which each bonding scheme is realized. Continue to assign single and double bonds as far as they are uniquely determined within each scheme, and delete the assigned bonds. The resulting systems (right column of Fig. 7) have the numbers of Kekulé structures k_1, k_2, k_3 and k_4, respectively, for the four schemes in question. The total K number, taking the multiplicities into account, is then determined as

$$K = k_1 + k_2 + 3k_3 + 3k_4, \qquad (7)$$

which in our example gives $K = 54$ for C_1.

A general treatment of primitive coronoids with trigonal symmetry makes it necessary to introduce certain fragments of U, the single chain

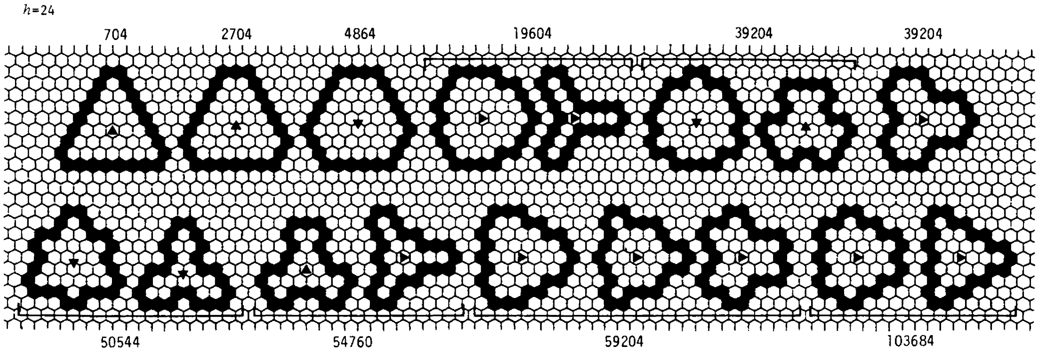

Fig. 6. All primitive coronoids of symmetry D_{3h} (▲) and $h=24$. K numbers are given. Bracketed systems are isoarithmic.

as defined above. Let u_0 be the chain obtained from U by deleting one hexagon from each side. Let u_1 and u_2 be the chains obtained from U by deleting one hexagon from one of the sides and a whole segment from the other in the two possible ways. Finally, let u_3 be the chain obtained from U by deleting one segment from each side. The number of Kekulé structures for a fragment u_i shall be identified by the symbol u_i ($i = 0, 1, 2, 3$). With this notation we obtain the result

$$k_1 = u_3^3 + 1,\ k_2 = u_0^3 + 1,$$
$$k_3 = u_0u_1u_2,\ k_4 = u_1u_2u_3 \tag{8}$$

and consequently

$$K = u_0^3 + u_3^3 + 3(u_0 + u_3)u_1u_2 + 2 \tag{9}$$

In this equation u_1u_2 may be eliminated by means of the theorem[28]

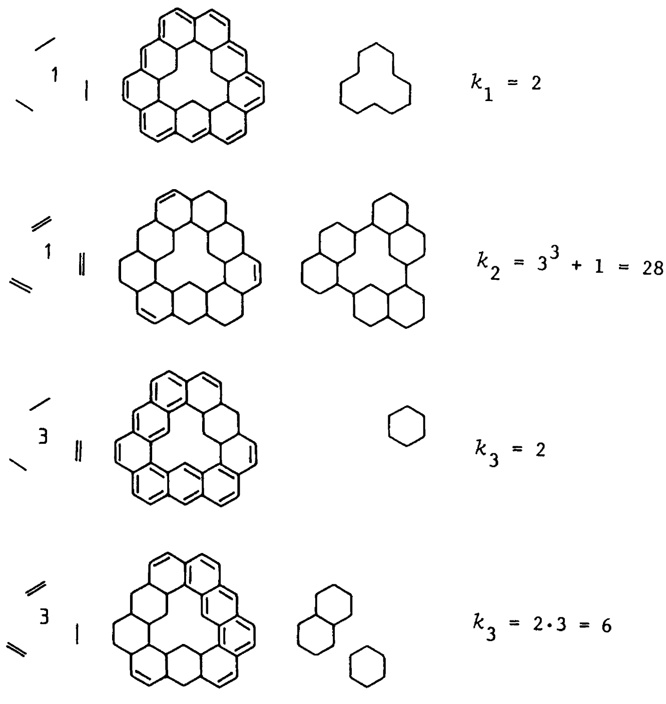

Fig. 7. The symmetry-adapted method of fragmentation applied to C_1.

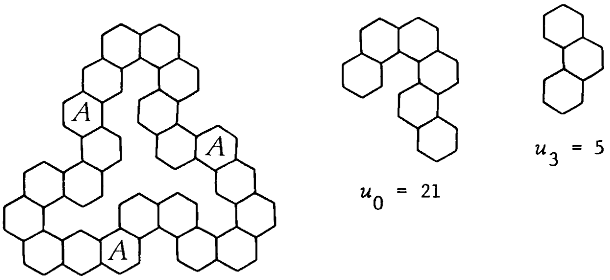

Fig. 8. A primitive coronoid of trigonal symmetry. Three symmetrically equivalent corners (A) have been selected, and the corresponding fragments u_0 and u_3 are shown. Their numbers of Kekulé structures are given.

$$u_0u_3 - u_1u_2 = \pm 1 \tag{10}$$

where the upper and lower sign apply to an even or odd number of segments, respectively. In our case, i.e. for U as a unit of a primitive coronoid of trigonal symmetry, it was stated that the number of segments is always even. Hence, eqn. (9) becomes

$$K = x^3 - 3x + 2 \tag{11}$$

where

$$x = u_0 + u_3. \tag{12}$$

In the case when U only holds two segments (as in C_1), the fragment u_3 degenerates to no hexagons; u_3 should then be set equal to 1.

One combinatorial K formula for a simple class of coronoids with trigonal symmetry (to which C_1 belongs) has been published before, viz.[21]

$$K\{/a + 1, b + 1/^3\} = ab(ab + 3)^2 + 4. \tag{13}$$

It pertains to a hollow hexagon with segments of alternating lengths $a + 1$ and $b + 1$; the total number of hexagons is $h = 3ab$. We find that (13) is a special case of (11). One has to use $u_0 = ab + 1$ and $u_3 = 1$. Hence $x = ab + 2$, which inserted into (11) gives an equation equivalent to (13).

As another illustrative example, consider the last system of Fig. 5; it is one of the seven existing systems characterized by $/3, 2^5/^3$. Fig. 8 explains some details, which result in $x = 21 + 5 = 26$. Here the appropriate fragments could be chosen so that they consist of all-kinked single chains, i.e. zigzag chains or their isoarithmic systems. For such systems it has long been known that the numbers of Kekulé structures coincide with the Fibonacci numbers.[16, 48] That gives readily u_0 and u_3 as F_7 and F_4, respectively, where $F_0 = F_1 = 1$, and

$$F_{n+2} = F_{n+1} + F_n \tag{14}$$

The numerical values of u_0 and u_3 are given in Fig. 8. Finally, we compute $K = 17500$ on inserting $x = 26$ into (11). The result is consistent with the appropriate number found in Fig. 5.

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