curve. If this transition is moved, restricted in size, or removed completely, the resulting fit is poor. We conclude that what appears to be a single B transition may in fact still arise from the two separate B_1 and B_2 transitions.

The curve-fitting results for RBC membranes at 310 imOsm, pH 8.15 (Figure 3), give another interpretation. Here also the B_1 and B_2 transitions appear to have merged on the temperature axis, resulting in a single B transition. Brandts et al.[8] demonstrated that the B_2 transition is very sensitive to pH, shifting to lower temperature as the pH is increased. According to their study, at 310 imOsm, pH 8.15, the B_2 transition nearly coincides on the temperature axis with the B_1 transition. This results in a single apparent transition near 57 °C, which our data also suggest in view of the simulation studies.

In conclusion, this technique offers a simple and rapid method to aid in fitting and resolving overlapping DSC transitions by use of a nonlinear regression program and Gaussian curves for the transitions. This ability offers the possibility of extracting more information from DSC scans which otherwise may have been overlooked.

ACKNOWLEDGMENT

We thank Dr. Roger L. Schnaare for his assistance with PCNONLIN. The work reported here is based wholly upon research performed in partial fulfillment of the requirements for the degree of doctor of philosophy in pharmaceutics at the Philadelphia College of Pharmacy and Science.

REFERENCES AND NOTES

(1) Metzler, C. M.; Weiner, D. L. *PCNONLIN User's Guide*; Statistical Consultants, Inc.: Lexington, KY, 1985; Vol. A.
(2) Jackson, W. M.; Brandts, J. E. *Biochemistry* **1970**, *9*, 2294-2301.
(3) Tsong, T. Y.; Hearn, R. P.; Wrathall, D. P.; Sturtevant, J. M. *Biochemistry* **1970**, *9*, 2666-2677.
(4) Tsalkova, T. N.; Privalov, P. L. *J. Mol. Biol.* **1985**, *181*, 533-544.
(5) Brandts, J. F.; Jackson, W. M.; Ting, T. Y. *Biochemistry* **1974**, *13*, 3595-3600.
(6) Elson, E.; Rewd, T. *Biopolymers* **1974**, *13*, 797-824.
(7) Brandts, J. F.; Erickson, L.; Lysko, K.; Schwartz, A. T.; Taverna, R. D. *Biochemistry*, **1977**, *16*, 3450-3454.
(8) Brandts, J. F.; Taverna, R. D.; Sadasivan, E.; Lysko, K. A. *Biochim. Biophys. Acta* **1978**, *512*, 566-578.
(9) Farach, M. C.; Martinez-Carrion, M. *J. Biol. Chem.* **1983**, *258*, 4166-4170.
(10) Stein, J. M. in *Molecular Association in Biological and Related Systems*; Gould, R. F., Ed.; American Chemical Society: Washington, DC, 1968; p 259.
(11) Freire, E.; Biltonen, R. L. *Biopolymers* **1978**, *17*, 463-479.
(12) Freire, E.; Biltonen, R. L. *Biopolymers* **1978**, *17*, 497-510.
(13) Snow, J. W.; Brandts, J. F.; Low, P. S. *Biochim. Biophys. Acta* **1978**, *512*, 579-591.
(14) Marwaha, L. K.; Tirrell, D. A. in *Biological Activities of Polymers*; Carraher, C. E., Gerelein, C. G., Eds.; American Chemical Society: Washington, DC, 1982; pp 163-175.
(15) Snow, J. W.; Vincentelli, J.; Brandts, J. F. *Biochim. Biophys. Acta* **1981**, *642*, 418-428.
(16) Dodge, J. T.; Mitchell, C.; Hanahan, D. J. *Arch. Biochem. Biophys.* **1963**, *100*, 119-130.
(17) Davio, S. R.; Low, P. S. *Biochemistry* **1982**, *21*, 3585-3593.
(18) Hook, T. M., Jr.; Silbellman, J. A. *Biopolymers* **1970**, *9*, 1319-1348.
(19) Fletcher, R.; Powell, M. J. D. *Comput. J.* **1963**, *6*, 163-168.
(20) Knorr, F. J.; Thorshein, H. R.; Harris, J. M. *Anal. Chem.* **1981**, *53*, 821-825.
(21) Rosenbaum, M.; Hancil, V.; Kromers, R. *J. Chromatogr.* **1980**, *191*, 157-167.
(22) Agard, D. A.; Steinberg, R. A.; Stroud, R. N. *Anal. Biochem.* **1981**, *111*, 257-268.
(23) Mastrangelo, S. V. R.; Dornte, R. W. *J. Am. Chem. Soc.* **1955**, *77*, 6200-6201.
(24) Albon, N.; Sturtevant, J. M. *Proc. Natl. Acad. Sci. U.S.A.* **1978**, *75*, 2258-2260.
(25) Orlov, S. N.; Shnyrov, V. L.; Zhadan, G. G.; Litvinov, I. S.; Gulak, P. V.; Pokudin, N. I.; Postnov, Y. V. *Bull. Exp. Biol. Med.* **1983**, *96*, 55-56.

Search for Concealed Non-Kekuléan Benzenoids and Coronoids

S. J. CYVIN,* J. BRUNVOLL, and B. N. CYVIN

Division of Physical Chemistry, The University of Trondheim, N-7034 Trondheim-NTH, Norway

Received February 14, 1989

Benzenoid and coronoid systems consist of congruent regular hexagons. A concealed non-Kekuléan benzenoid or coronoid is a system that does not possess any Kekulé structure ($K = 0$) and yet has $\Delta = 0$, where Δ is the color excess. The systematic search for concealed non-Kekuléan benzenoids is reviewed and supplemented by some of the smallest such systems with trigonal symmetry. An original systematic search for the smallest concealed non-Kekuléan coronoids is reported. This search resulted in 23 such systems with $h = 15$, where h is the number of hexagons. The theory of segmentation, which has been developed for benzenoids, is applied to coronoids for the first time. Finally, the smallest concealed non-Kekuléan double coronoid (two corona holes) is identified.

INTRODUCTION

The perfect matchings of benzenoid graphs correspond to the Kekulé structures of benzenoid (polycyclic aromatic) hydrocarbons. It is recognized that these notions have great chemical importance and mathematical interest.[1] Benzenoid systems[1-3] (or simply benzenoids), which have chemical counterparts in benzenoid hydrocarbons, are planar geometrical constructions consisting of congruent regular hexagons. Here "planar" is taken in the geometrical sense, and it is implied that helicenic systems are excluded. For the sake of simplicity one also speaks about Kekulé structures for benzenoid systems. Benzenoids that do not possess any Kekulé structure are called non-Kekuléan, otherwise, Kekuléan.

Sometimes in the following we shall designate a benzenoid system B. The Kekulé structure count (number of Kekulé structures) of B is denoted K.

It is well-known that benzenoid graphs are bipartite; all vertices can be colored by two colors (say, black and white) so that two adjacent vertices never have the same color. Black and white vertices correspond to starred and unstarred[4,5] (or marked and unmarked[6]) carbon atoms.

The color excess (or Δ value) is an important invariant for benzenoid systems. The quantity Δ is defined as the absolute magnitude of the difference between the numbers of black and white vertices, say $n^{(b)}$ and $n^{(w)}$, respectively. In other words

$$\Delta = |n^{(b)} - n^{(w)}| \qquad (1)$$

0095-2338/89/1629-0236$01.50/0

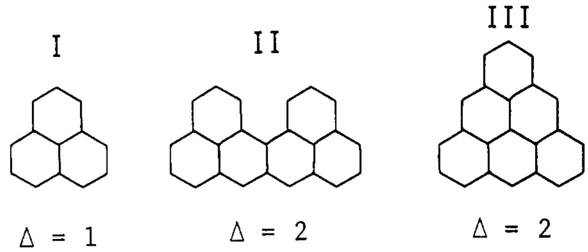


Figure 1. Three obvious non-Kekulêan benzenoids with the Δ values (color excess) indicated.

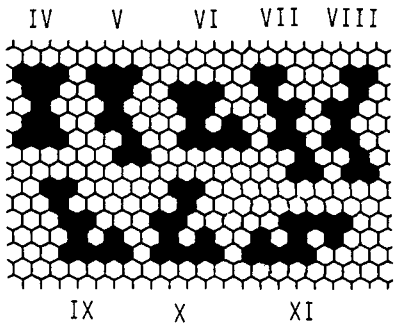


Figure 2. Eight smallest (11 hexagon) concealed non-Kekulêan benzenoids.

It is long known (and obvious) that any Kekulêan benzenoid must have the same number of black and white vertices. Therefore, if B is Kekulêan, then $\Delta = 0$. However, this is *not* a necessary *and* sufficient condition for B to be Kekulêan. It has been demonstrated that non-Kekulêan benzenoids with $\Delta = 0$ can be constructed. Such systems ($K = 0$, $\Delta = 0$) have been termed concealed non-Kekulêans,[7] while the non-Kekulêan ($K = 0$) benzenoids with $\Delta > 0$ are the obvious non-Kekulêans.

Phenalene (benzo[*de*]naphthalene, I), dibenzo[*de,hi*]-naphthacene (II), and Clar's hydrocarbon (triangulene, III) are well-known examples of obvious non-Kekulêan benzenoids[1,6] (see Figure 1).

A benzenoid hydrocarbon corresponding to a concealed non-Kekulêan was probably described for the first time by Clar.[6] He constructed the system IV of Figure 2 and pointed out that it has no Kekulê structure, but 19 marked and 19 unmarked carbon atoms; hence, $n^{(b)} = n^{(w)}$ and $\Delta = 0$. On the basis of a theory on para bonds Clar[6] predicted that IV should be possible to synthesize and should yield a stable diradical. These expectations have so far not been fulfilled.

In the present work we summarize the search for the interesting systems called concealed non-Kekulêans. They have been constructed by trial and error, by computerized generations, and finally by graph-theoretical deductions. Also, a number of original results from computer generations are reported.

A coronoid system[8] (or simply "coronoid") is a "benzenoid with a hole". These systems have also been called "(true) circulenes"[9,10] among other designations. The notions Kekulêan as well as obvious and concealed non-Kekulêan are also applicable to coronoids. Figure 3 shows three examples of obvious non-Kekulêan coronoid systems.

The concealed non-Kekulêan coronoids have hardly been studied systematically before. Here we report, among other results, the generation of all the smallest systems of this category.

SMALLEST CONCEALED NON-KEKULÊAN BENZENOIDS

Historical. A systematic search for concealed non-Kekulêan benzenoids seems to have started in 1974 with Gutman,[11] who

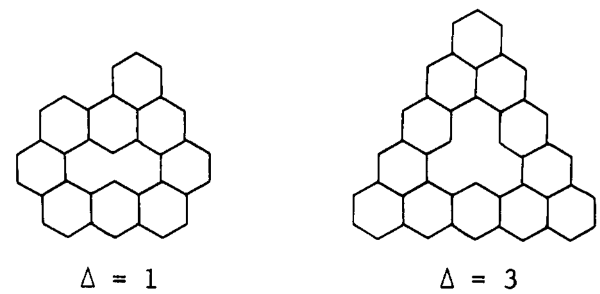


Figure 3. Three obvious non-Kekulêan coronoids with Δ values indicated.

depicted two of these systems by trial and error. One of them, viz., IV, is the same as the one of Clar[6] (see above), while the other, VII (see Figure 2), was a new discovery. These two systems have $h = 11$, where h is used to designate the number of hexagons. Another original contribution by Gutman[11] was his claim that no concealed non-Kekulêan benzenoid with $h < 11$ can be constructed. On the other hand, he did not claim that IV and VII are the only smallest ($h = 11$) concealed non-Kekulêans. A new system of this catagory, viz., XI, appeared in 1981 in a paper by Balaban.[12] It was followed 1 year later by four additional representatives, viz., VI, VIII, IX, and X, in a work by the same author.[13] Not before 1986 was the last system from the set of Figure 2, viz., V, detected and reported by Hosoya.[14] He was the first to publish the whole set of these eight $h = 11$ concealed non-Kekulêan benzenoids (Figure 2). The system V was also found independently by Cyvin and Gutman,[7] who published the same eight concealed non-Kekulêans (Figure 2) 1 year after Hosoya.

Hosoya[14] based his constructions on inactive V-regions for obvious non-Kekulêans, which were used as building stones for the concealed non-Kekulêans. Cyvin and Gutman[7] just resorted to trial and error. In neither of these works was it claimed explicitly that the eight constructed systems are the only concealed non-Kekulêans with $h = 11$.

In 1987 it was definitely proved, by independent computer programming in People's Republic of China and Norway, that there are exactly eight concealed non-Kekulêan benzenoids with $h = 11$.[15]

One or, more frequently, both of the Gutman[11] examples (IV and VII) have been used or quoted many times in different contexts.[1,2,13,16–22] In the most recent works it has become popular to quote the whole set of eight systems (Figure 2).[23–25]

Computer Programming. All the 30 086 benzenoid systems with $h = 10$ were computer-generated for the first time by the Düsseldorf–Zagreb group.[10,26,27] Since then this number has been reproduced several times in different places, and the $h \leq 10$ benzenoids are rather well known and classified.[28,29] Therefore, it was a relatively easy task to ascertain by computer programming[15,28,29] that there are no concealed non-Kekulêans among the $h = 10$ benzenoid systems, thus confirming Gutman's[11] original claim to this effect.

The Chinese approach to the problem with $h = 11$[15] was a complete generation of these benzenoid (and coronoid) systems, whereafter the 8 concealed non-Kekulêans could be recognized among the whole set of 141 229 benzenoids (+283 coronoids).[28] In Norway an entirely different approach was used.[15] It was based on a principle referred to as sifting. Below, the method is described in some detail because the same principle was used in the present work on coronoids. To give a most instructive description of the sifting, we have taken the liberty to deviate in some details from the procedures actually used in the practical solution of the problem.

A crucial point of the procedure is the possibility to determine the Δ value for a generated benzenoid. This is accomplished most easily, either by sight or in computer programming, by counting the peaks and valleys.[7,16] A peak

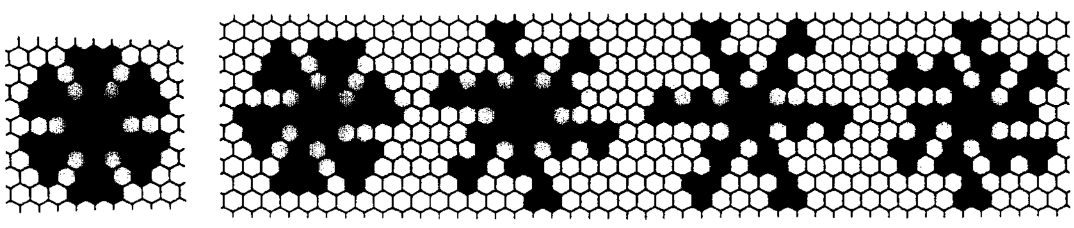


Figure 4. Five smallest (h = 43) concealed non-Kekuléan benzenoids with hexagonal symmetry.

(valley) is a vertex of second degree pointing to the north (south). Then the convention is adopted that the benzenoid system should have some of its edges vertical (north–south). Let the numbers of peaks and valleys in a given orientation (there may at most be three nonequivalent orientations in consistence with the above convention) be denoted n_p and n_v, respectively. Then

$$\Delta = |n_v - n_p| \quad (2)$$

is independent of the orientation. It has been proved[7] that the Δ of eq 2 is the invariant identical with the same quantity of eq 1, the color excess.

Suppose now that all the benzenoid systems with h = 10 have been classified according to the Δ values. It appears that they count 14 107 and 14 024 systems[28] with Δ = 0 and Δ = 1, respectively. Denote these sets by B_0 and B_1, where the subscripts refer to the Δ values. Now all the concealed non-Kekuléans with h = 11 will certainly be generated among the systems obtained by (A) adding one hexagon at a time to all benzenoids in B_0, using the one-, three- and five-contact additions, and (B) adding one hexagon at a time to all benzenoids in B_1, using the two- and four-contact additions. Here a k-contact addition refers to the number of edges (k) that the added hexagon gets in common with the original benzenoid. Let us inspect the two sets of additions separately.

Set A. According to the selection rules for Δ[30] we know that the Δ value does not change from the original (h = 10) benzenoids and therefore remains as Δ = 0. We also know that normal benzenoids subjected to the appropriate additions result in new normal benzenoids. Therefore, it is sufficient to select the essentially disconnected benzenoids from the set B_0. We recall that an essentially disconnected benzenoid is a Kekuléan with fixed bonds (single or double) in all Kekulé structures, while the other Kekuléans are normal.[22,27] Therefore, the number of benzenoids in B_0 can be reduced drastically to 3732.

Set B. The specified additions to the benzenoids in B_1 make the Δ value shift by ±1.[30] Therefore, the generated benzenoids will either have Δ = 0 or Δ = 2, of which those with Δ = 2 immediately can be discarded as a part of the sifting.

In both cases A and B, as the main idea of the sifting, all the generated systems are not stored. Every time a new system with Δ = 0 is generated, it is tested for the Kekulé structure count. If $K > 0$, which happens in the great majority of the cases, then the system is discarded. If $K = 0$, then it is stored. Thus, there will always be a very small number of benzenoids (not greater than eight), for which a comparison must be executed to eliminate duplicated (isomorphic) systems. Of course, the results from A and B must finally be assembled. One ends up with all nonisomorphic h = 11 benzenoids with Δ = 0 and K = 0; they are the concealed non-Kekuléans.

Mathematical Deduction. Zhang and Guo[31] proved recently by stringent graph-theoretical methods that the eight systems depicted in Figure 2 are the only smallest (h = 11) concealed non-Kekuléan benzenoids. We shall not go into details of their proof, which invokes fragments of the benzenoids. In a subsequent section we shall report another result from the same work concerning the $h \leq 14$ concealed non-Kekuléans.

LARGER CONCEALED NON-KEKULÉAN BENZENOIDS

Systems with 12 and 13 Hexagons. The computer analyses in China and Norway[15] were pursued to the corresponding treatments of benzenoids with h = 12.[32] It was deduced that among the totality of 669 584 systems[29] there are exactly 98 concealed non-Kekuléan benzenoids.

Quite recently Guo and Zhang,[33] in continuation of their graph-theoretical analyses,[31] came to the same conclusion of 98 concealed non-Kekuléan benzenoid systems with h = 12. Furthermore, they deduced as an original contribution the number 1097 for all concealed non-Kekuléans with h = 13.

Supplementary References. Concealed non-Kekuléan benzenoids with more than 11 hexagons have been considered in many of the above-cited works[7,13,14,16,19,20,22,23,31-33] and elsewhere.[34-38]

In the systematic studies of regular t-tier (3-tier,[39] 4-tier,[39] 5-tier,[37] and 6-tier[23]) strips some classes referred to as goblets are encountered. They are either essentially disconnected or concealed non-Kekuléan. The first system of Figure 2 (IV) is a goblet, and several larger goblets are treated in some of the cited works.

Several of the above-cited papers contain theoretical studies on the conditions for a benzenoid to be Kekuléan or non-Kekuléan. This is not the place to survey the numerous theorems that have been developed in this area, especially because a recent, comprehensive review dealing with this topic is available.[22] Nevertheless, we shall in the next section explain the concept of segmentation[7,16] and in this connection quote a simple, sufficient condition for a benzenoid to be non-Kekuléan. This will be useful for subsequent parts of the present work, where the same methods are adapted to coronoids for the first time.

In two of the above references[24,32] the concealed non-Kekuléan benzenoids (and coronoids) with hexagonal symmetry have been treated. Additional works on concealed non-Kekuléans with specific symmetries have been reported, and some original contributions are supplied in the present work.

CONCEALED NON-KEKULÉAN BENZENOIDS WITH SPECIFIC SYMMETRIES

Hexagonal Symmetry. A concealed non-Kekuléan benzenoid of regular hexagonal (D_{6h}) symmetry was given for the first time in 1986 by Hosoya.[40] This system, which has 43 hexagons, is found in Figure 4 as XII. Hosoya conjectured that this is the smallest system of that kind. The same year[41] this conjecture was verified by a computer analysis. More precisely, it was found that the smallest concealed non-Kekuléan belonging to the D_{6h} symmetry is a unique system with h = 43, while four such systems of the C_{6h} symmetry and h = 43 can be constructed, viz., XIII–XVI of Figure 4; instead of the above reference[41] some less obscure publications may be consulted.[24,32,42] Three of the C_{6h} systems had been produced earlier[43] by trial and error.

It would be quite inconceivable to obtain the above conclusions from a complete enumeration of benzenoids up to the

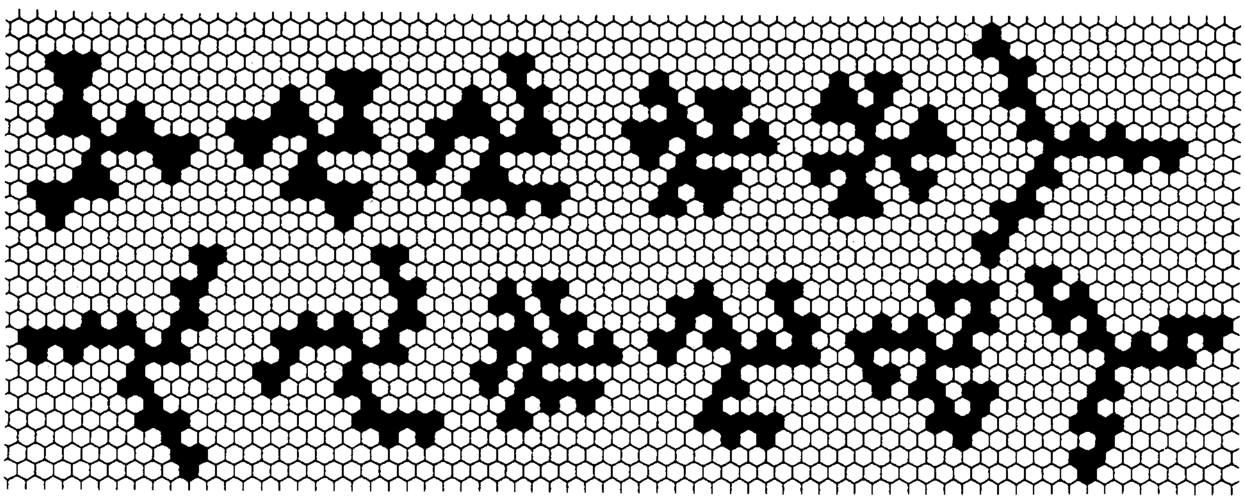


Figure 5. Twelve concealed non-Kekuléan benzenoids of symmetry C_{3h} and $h = 34$.

Table I. Numbers of Benzenoids with Hexagonal Symmetry

	concealed non-Kekuléan		total	
h	D_{6h}	C_{6h}	D_{6h}	C_{6h}
1	0	0	1^{a}	0
7	0	0	$1^{a,b}$	0
13	0	0	$2^{a,b}$	0
19	0	0	$2^{a,b}$	$2^{a,b}$
25	0	0	3^{b}	8^{b}
31	0	0	5^{b}	32^{b}
37	0	0	8^{b}	128^{b}
43	$1^{b,c}$	$4^{b,c}$	13^{b}	527^{b}
49	0^{d}	42^{d}	20^{b}	2209^{b}
55	1^{e}	312^{e}	35^{b}	9470^{b}
61	1^{f}		$60^{f,g}$	
67	4^{f}		$104^{f,g}$	
73	7^{f}		$183^{f,g}$	

[a] Reference 28. [b] Reference 42. [c] Reference 41. [d] Reference 32. [e] Reference 44. [f] Reference 24. [g] Reference 29.

Table II. Numbers of Benzenoids with Trigonal Symmetry[a]

h	D_{3h}	C_{3h}	h	D_{3h}	h	D_{3h}
3	1	0	21	10	34	557
4	1	0	22	41	36	164
6	1	1	24	16	37	1050
7	1	1	25	72	39	286
9	1	5	27	28	40	2154
10	4	5	28	149	42	557
12	3	21	30	50	43	4142
13	4	26	31	272	45	998
15	3	95	33	87	46	8537
16	12	118				
18	6	423				
19	19	543				

[a] Data for $h < 20$ from ref 28. The others are present results.

actual h value. One example shows how sparsely the systems with hexagonal symmetry are distributed among the totality of the benzenoids: among the 849 285 benzenoid systems with $h \leq 12$[29] there are 2 with hexagonal symmetry (benzene and coronene). Fortunately, a specific generation of the systems with hexagonal symmetry is feasible. These benzenoids occur at $h = 1, 7, 13, 19, 25, \ldots$. For $h = 43$ in particular, the five concealed non-Kekuléans could easily be recognized among a totality of only 540 systems.[42]

The generations and enumerations of benzenoids with hexagonal symmetry have been carried beyond $h = 43$ (see Table I). The relevant papers are supplied with numerous illustrations.[24,32,42,44]

Trigonal Symmetry. Table II gives a survey of the existing enumeration results[28] for benzenoids with trigonal symmetry, supplemented by original data.

It has been pointed out[45] that it is not easy to construct small concealed non-Kekuléan benzenoid systems with trigonal symmetry. The task is certainly easier for the systems with hexagonal symmetry, as may be understood from the following fact. Whereas all benzenoids with hexagonal symmetry have $\Delta = 0$,[42] those with $\Delta > 0$ are most abundant among the benzenoids with trigonal symmetry. To be precise, there are, for instance, among the 1294 systems with $h < 20$ (cf. Table II) 456 benzenoids with $\Delta = 0$ and 838 obvious non-Kekuléan with $\Delta > 0$.[45]

It was ascertained by the computer analysis that there are no concealed non-Kekuléan benzenoids of trigonal symmetry with $h < 20$. In the previous work[45] two concealed non-Kekuléans with $h = 34$ were constructed by annelating three identical smallest concealed non-Kekuléans (cf. Figure 2) to benzene. In Figure 5 we show 12 representatives of this kind, being well aware of the fact that the list is not complete. Still worse, it has not been proved whether these systems with $h = 34$ are among the smallest concealed non-Kekuléan benzenoids with trigonal symmetry. On the other hand, they are the smallest we were able to find by trial and error. All of the systems in Figure 5 and others that may be constructed by the same principles belong to the symmetry group C_{3h}.

The accessible computer capacity did not allow us to determine the smallest C_{3h} concealed non-Kekuléans by computerized generations of the benzenoids. To shed some light into the problem from another viewpoint, we concentrated upon the regular trigonal (D_{3h}) systems. This analysis met with success inasmuch as we were able to detect the smallest concealed non-Kekuléans with D_{3h} symmetry.

The oscillating enumeration data for benzenoids with D_{3h} symmetry (cf. Table II) may seem confusing. Things become comprehensible when it is recalled that the benzenoids in question are subdivided into (i) benzenoids with trigonal symmetry of the first kind and (ii) benzenoids of trigonal symmetry of the second kind.[46] These systems are characterized by having (i) a hexagon in the center and (ii) a vertex in the center, respectively. Furthermore, they occur for (i) $h = 4, 7, 10, 13, 16, \ldots$ and (ii) $h = 3, 6, 9, 12, 15, \ldots$, respectively. It has been proved[46] that all benzenoids of trigonal symmetry of the second kind are obvious non-Kekuléan systems. Therefore, as far as the concealed non-Kekuléan benzenoids are concerned, we only need to consider the systems of the first kind. Table III shows the relevant classification of these systems for $h > 20$, which was executed by the computer analysis. The subdivision of the D_{3h} systems into types a and b is characterized by (a) the presence of a horizontal twofold symmetry axis or (b) a vertical twofold symmetry axis.

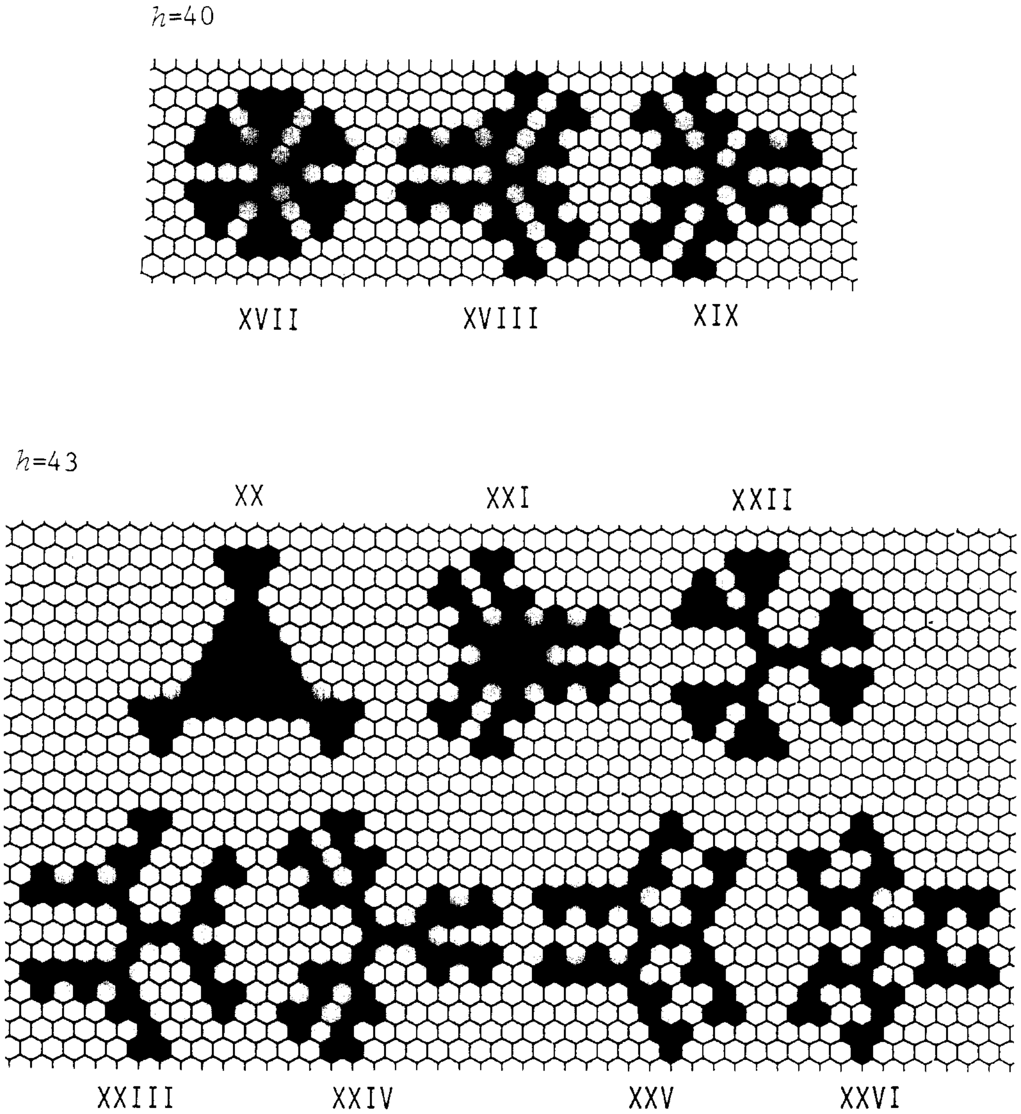


Figure 6. Smallest ($h \leq 43$) concealed non-Kekulêan benzenoids with regular trigonal symmetry (D_{3h}).

Table III. Subdivided Numbers of Benzenoids with $h > 20$ and Regular Trigonal (D_{3h}) Symmetry

	concealed non-Kekulêan		total	
h	D_{3h}(ia)	D_{3h}(ib)	D_{3h}(ia)	D_{3h}(ib)
22	0	0	36	5
25	0	0	64	8
28	0	0	133	16
31	0	0	247	25
34	0	0	507	50
37	0	0	965	85
40	3	0	1988	166
43	6	1	3846	296
46	34	0	7958	579

Under this definition we adhere to the convention that the benzenoid system is oriented so that some of its edges are vertical.

The computer analysis revealed three concealed non-Kekulêan benzenoids among the 2154 systems of D_{3h} symmetry with $h = 40$; they are the smallest systems of this category. The forms are given in the top row of Figure 6 (XVII–XIX). All of them are of the type ia. Furthermore, each of them is found to be composed of three identical units of concealed non-Kekulêan benzenoids annelated to benzene. They have this property in common with the systems of Figure 5, but in the present case the units are not among the smallest ($h = 11$) concealed non-Kekulêans but possess 13 hexagons each. This property of the smallest concealed D_{3h} non-Kekulêans may be taken as an indication that the C_{3h} systems of Figure 5 really are the smallest concealed non-Kekulêans with trigonal symmetry whatsoever. However, a definite proof is still awaited.

Figure 6 (XX–XXVI) includes the forms of the $h = 43$ concealed non-Kekulêan benzenoids belonging to D_{3h}. The first of these systems (viz., XX) is an interesting discovery: it is the smallest concealed non-Kekulêan belonging to the ib category.

SEGMENTATION OF BENZENOIDS

Definitions. Assume again that a benzenoid system B is oriented so that some of its edges are vertical. An (elementary) edge cut is a horizontal line through a number of edges, where both of the end edges belong to the perimeter. The cut edges are called tracks. The horizontal line divides B into an upper and a lower segment. It is noted that the two segments are not actually separated from each other.

Let the numbers of peaks and valleys in the upper segment be denoted by n_p' and n_v', respectively. Corresponding notation for the lower segment are n_p'' and n_v''.

Assume that the benzenoid B has $\Delta = 0$. Let s denote the partial difference between the numbers of peaks and valleys, viz.

$$s = n_p' - n_v' = n_v'' - n_p'' \qquad (3)$$

The last equality holds by virtue of the relation $n_p' + n_p'' =$

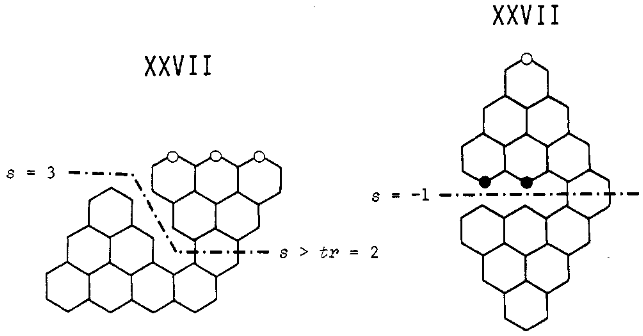


Figure 7. Concealed non-Kekulêan benzenoid used to illustrate the conditions (4). Peaks and valleys of the upper segment are indicated by white and black circles, respectively.

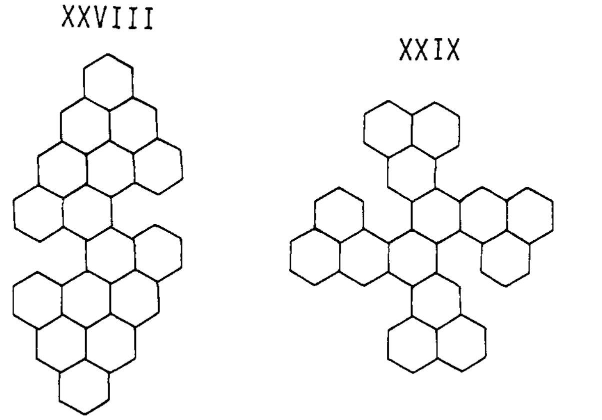


Figure 8. Two concealed non-Kekulêan benzenoids of type I.

$n_v' + n_v''$ in consistence with eq 2 for $\Delta = 0$; hence, $n_p = n_v$. The number of tracks is denoted by tr.

Theorem.[7,16] If one finds

$$s > \text{tr} \quad \text{or} \quad s < 0 \qquad (4)$$

for a certain segmentation of B, then B is a (concealed) non-Kekulêan benzenoid.

An obvious non-Kekulêan is easily recognized by counting the peaks and valleys with the result $n_p \neq n_v$. Therefore, we maintain the assumption that $n_p = n_v$ or $\Delta = 0$ in the following. Then either of the conditions (eq 4) is sufficient for B to be a concealed non-Kekulêan. This rule for recognizing concealed non-Kekulêan benzenoids is very useful inasmuch as it is usually a conceivable task to inspect all possible segmentations. By such a systematic search one should observe that at most three orientations of B should be inspected. This number is lowered if B is symmetrical, i.e., if it has more than the trivial symmetry plane through all vertices. It should also be clear that it is profitable to choose a segmentation with a minimum number of tracks. Figure 7 shows a benzenoid (XXVII) in two orientations. The first and second condition of eq 4 are realized for one segmentation in each orientation.

Further Developments. In all the examples of concealed non-Kekulêan benzenoid systems in the preceding sections it is possible to find segmentations where $s >$ tr. The question has been posed[7,16] whether this condition, or at least one of the conditions in eq 4, is sufficient *and* necessary for a benzenoid to be a concealed non-Kekulêan. Several counterexamples have been produced (see, e.g., the cited review[22]) demonstrating that this is not the case. A fairly small example[7] ($h = 16$) is shown as XXVIII in Figure 8.

The most profound analysis of the above question is from Zhang and Guo.[31] They referred to a concealed non-Kekulêan benzenoid where neither of the conditions (eq 4) can be realized for any segmentation as being of type I. Furthermore, they proved mathematically that the smallest concealed non-Kekulêan of type I is a unique system with $h = 14$. This

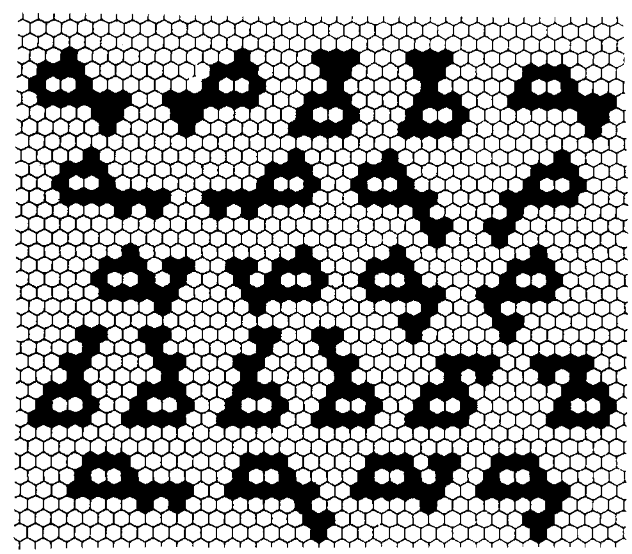


Figure 9. Twenty-three smallest ($h = 15$) concealed non-Kekulêan coronoid systems (with a naphthalenic hole).

system, XXIX, is depicted in Figure 8.

SMALLEST CONCEALED NON-KEKULÊAN CORONOIDS

The notion of color excess (Δ) is applicable to coronoids as well as benzenoids and defined in the same way by eq 1. Also, eq 2 is valid for this quantity in coronoids. Here one should observe that the peaks and valleys on the inner perimeter (inside the hole) also must be counted if they exist. A concealed non-Kekulêan coronoid is defined precisely as for benzenoids by $K = 0$, $\Delta = 0$.

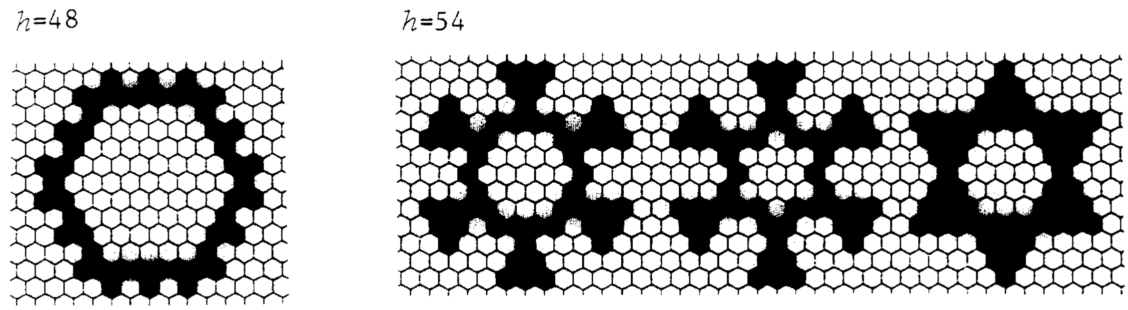
In the first work[8] where the existence of concealed non-Kekulêan coronoids was pointed out, several examples, obtained by trial and error, are depicted. The three smallest systems found have $h = 15$. However, it was not claimed that they really are among the smallest obvious non-Kekulêan coronoid systems.

In the present work we solved this question by computer programming in the same way as was done for benzenoids (see above). The selection rules for Δ are valid for coronoids as well as the benzenoids, so that the method of sifting is applicable in the form as it was described.

In this analysis we made the basic assumption that the smallest concealed non-Kekulêan coronoid has a naphthalenic (2-hexagon) hole. This seems to be a plausible assumption. If it does not hold, we have at least generated all the smallest concealed non-Kekulêan coronoids within the class of those with a naphthalenic hole.

The total numbers of coronoids with a naphthalenic hole and $h = 8$, 9, 10, and 11 are found elsewhere.[8] We have supplemented them by 1554, 9450, and 56 003 for $h = 12$, 13, and 14, respectively. A classification of all these coronoids assured that there are no concealed non-Kekulêan systems among them. Since our computer capacity did not allow us to enumerate and classify all the coronoids with $h = 15$, we set out to generate the concealed non-Kekulêans among them by sifting. All the $h = 15$ coronoids with $K = 0$, $\Delta = 0$ are certainly generated by (A) adding one hexagon at a time to the 22 154 systems with $h = 14$, $\Delta = 0$, using the one-, three- and five-contact additions, and (B) adding one hexagon at a time to the 26 919 systems with $h = 14$, $\Delta = 1$, using the two- and four-contact additions.

The described analysis resulted in exactly 23 concealed non-Kekulêan coronoid systems with $h = 15$. The forms are displayed in Figure 9. Each of them may be interpreted as an obvious non-Kekulêan coronoid with nine hexagons, to



XXX XXXI XXXII XXXIII

Figure 10. Four smallest ($h \leq 54$) concealed non-Kekulêan coronoids with regular hexagonal (D_{6h}) symmetry.

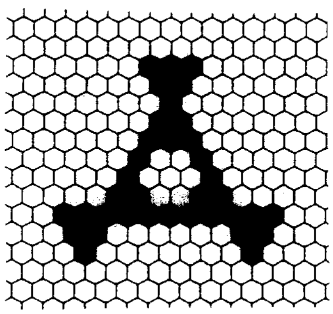


Figure 11. Concealed non-Kekulêan coronoid of trigonal symmetry.

which one of the fragments II or III (Figure 1) is condensed. All of them are of the C_s symmetry.

CONCEALED NON-KEKULÊAN CORONOIDS WITH SPECIFIC SYMMETRIES

Hexagonal Symmetry. In a recent work[24] the smallest concealed non-Kekulêan coronoids with regular hexagonal symmetry (D_{6h}) were detected by computer programming. First, it was ascertained that no such system exists for $h \leq 42$, with either D_{6h} or C_{6h} symmetry. Second, it was concentrated upon the D_{6h} systems for $h \geq 48$. It was found that there is exactly 1 concealed non-Kekulêan coronoid of D_{6h} with $h = 48$ (XXX); there are 3 with $h = 54$ (XXXI–XXXIII) and 20 with $h = 60$ (see Figure 10).

Trigonal Symmetry. So far, no systematic search for concealed non-Kekulêan coronoids of trigonal symmetry has been done. The system of Figure 11 emerges by creating a coronenic hole in the benzenoid XX (Figure 6). This coronoid has $h = 36$ and belongs to D_{3h}. It is quite possible that this system is (one of) the smallest concealed non-Kekulêan coronoid with trigonal symmetry. We have not been able to construct any smaller such system by trial and error.

SEGMENTATION OF CORONOIDS

The theory of segmentation may straightforwardly be adapted to coronoid systems.

A Kekulêan coronoid system (like a benzenoid) must have the same number of black and white vertices, which means that $\Delta = 0$. The peaks and valleys for a coronoid are to be counted on the inner perimeter as well as on the outer. Then eq 2 is valid also for coronoids. It may happen, for a given orientation, that there are no peaks or valleys on the inner perimeter.

We assume, for a coronoid, that $n_p = n_v$. Therefore, $\Delta = 0$, and if the system is non-Kekulêan, it is a concealed non-Kekulêan system.

The conditions (eq 4) are valid also for a coronoid system

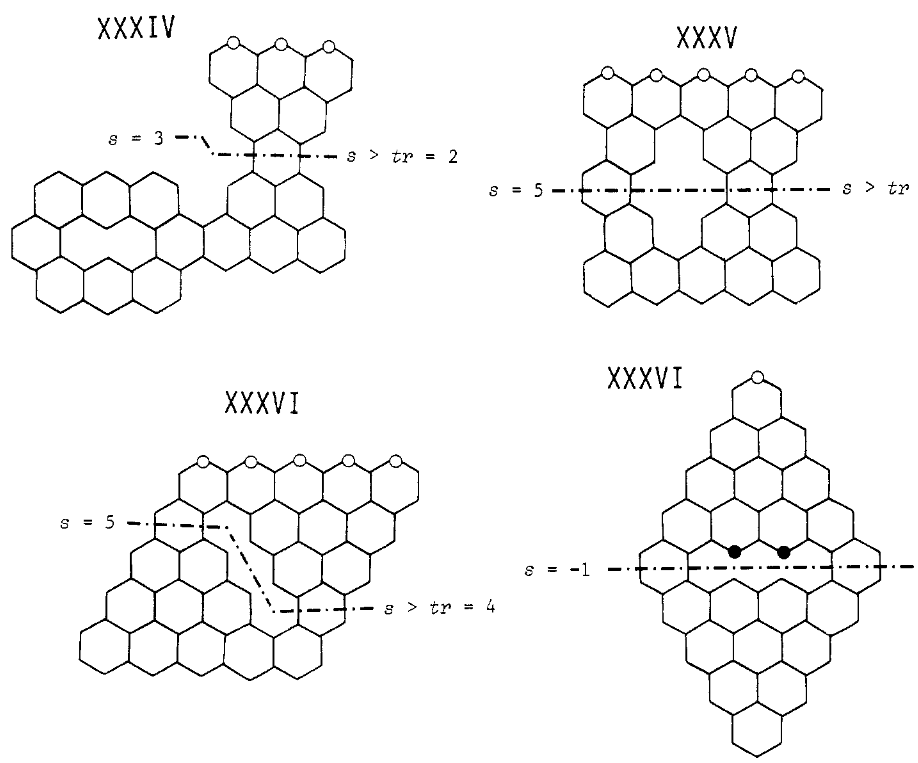


Figure 12. Concealed non-Kekulêan coronoids illustrating the conditions of segmentation.

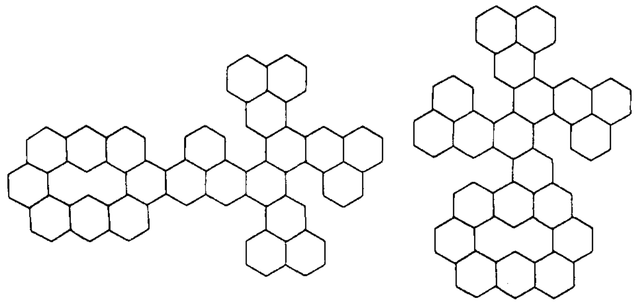


Figure 13. Two concealed non-Kekulêan coronoids of type I.

as sufficient conditions for the system to be (concealed) non-Kelulêan. This rule becomes more useful when we, in addition to an ordinary edge cut, make allowance for an edge cut through the corona hole. This is a line that cuts, in succession, edges on the outer, inner, inner, and outer perimeters. More edges may occasionally be cut between one or both pairs of the edges of the outer and inner perimeters. In these regions the line should be horizontal, but within the corona hole it may be parallel shifted.

Figure 12 shows some illustrations of the conditions eq 4. The system XXXIV is a rather trivial example, where a Kekulêan coronoid simple has been fused to the goblet IV, a concealed non-Kekulêan benzenoid. The condition $s >$ tr is realized by an ordinary edge cut through the benzenoid part of the system, not affecting the corona hole.

The next example (XXXV) is more interesting inasmuch as a cut through the corona hole is necessary to realize $s >$ tr. Finally, the figure shows a concealed non-Kekulêan coronoid (XXXVI) in two orientations. Both of the conditions (eq 4) are realized, each in one orientation. If the corona hole of XXXV is filled with hexagons, then the system becomes an essentially disconnected (Kekulêan) benzenoid. The coronoid XXXVI with the hole filled becomes a parallelogram, which is a normal (Kekulêan) benzenoid.

All the systems of Figure 9 are of the trivial kind, where $s >$ tr is achieved by an ordinary edge cut through the perylene unit. This is also the case for XXXI and XXXII (Figure 10) and the system of Figure 11. In the case of XXX and XXXIII, on the other hand, an edge cut through the center of the corona hole is necessary to attain $s >$ tr.

The interesting question occurs whether concealed non-Kekulêan coronoids of type I can be constructed, i.e., those where neither of the conditions (eq 4) can be realized for any segmentation in any orientation. Trivial examples readily come into one's mind, e.g., the two systems of Figure 13. Here a Kekulêan coronoid has been fused to XXIX (left) or compressed with XXIX (right). The two systems have $h = 22$ and $h = 20$, respectively.

DOUBLE CORONOIDS

So far it has been tacitly assumed that a coronoid is a system with only one hole. When allowance is made for more than one corona hole, we speak about multiple coronoids. Then the systems with one hole should, in more precise terms, be called single coronoids.

The smallest double coronoid (with two holes; see XXXVII of Figure 14) was mentioned, probably for the first time, by Dias,[47] who also depicted one of the smallest triple coronoids (three holes). These systems have 13 and 18 hexagons, respectively.

In a previous work by Brunvoll et al.[8] some concealed non-Kekulêan double coronoids were found, the smallest of them with 18 hexagons. In the present work we have deduced by computer enumerations that the smallest such system actually is a unique double coronoid with $h = 17$. It is found in Figure 14 (XXXVIII).

XXXVII XXXVIII

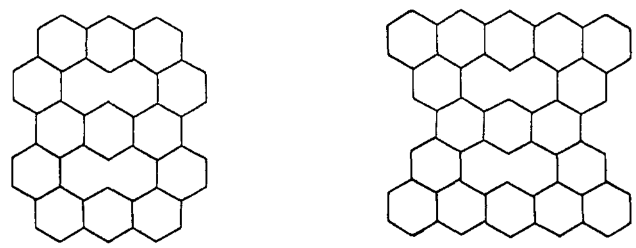


Figure 14. Smallest double coronoid ($h = 13$; left) and the smallest concealed non-Kekulêan double coronoid ($h = 17$; right).

ACKNOWLEDGMENT

Financial support to B.N.C. from The Norwegian Research Council for Science and the Humanities is gratefully acknowledged.

REFERENCES AND NOTES

(1) Trinajstić, N. *Chemical Graph Theory*; CRC Press: Boca Raton, FL, 1983; Vol. I, II.
(2) Gutman, I. *Bull. Soc. Chim. Beograd* **1982**, *47*, 453.
(3) Gutman, I.; Polansky, O. E. *Mathematical Concepts in Organic Chemistry*; Springer-Verlag: Berlin, 1986.
(4) Coulson, C. A.; Longuet-Higgins, H. C. *Proc. R. Soc. London* **1947**, *A192*, 16.
(5) Longuet-Higgins, H. C. *J. Chem. Phys.* **1950**, *18*, 265.
(6) Clar, E. *The Aromatic Sextet*; Wiley: London, 1972.
(7) Cyvin, S. J.; Gutman, I. *THEOCHEM* **1987**, *150*, 157.
(8) Brunvoll, J.; Cyvin, B. N.; Cyvin, S. J. *J. Chem. Inf. Comput. Sci.* **1987**, *27*, 14.
(9) Dias, J. R. *J. Chem. Inf. Comput. Sci.* **1982**, *22*, 15.
(10) Knop, J. V.; Szymanski, K.; Jeričević, Ž.; Trinajstić, N. *MATCH* **1984**, *16*, 119.
(11) Gutman, I. *Croat. Chem. Acta* **1974**, *46*, 209.
(12) Balaban, A. T. *Rev. Roum. Chim.* **1981**, *26*, 407.
(13) Balaban, A. T. *Pure Appl. Chem.* **1982**, *54*, 1075.
(14) Hosoya, H. *Croat. Chem. Acta* **1986**, *59*, 583.
(15) Brunvoll, J.; Cyvin, S. J.; Cyvin, B. N.; Gutman, I.; He, W. J.; He, W. C. *MATCH* **1987**, *22*, 105.
(16) Sachs, H. *Combinatorica* **1984**, *4*, 89.
(17) Balaban, A. T. *THEOCHEM* **1985**, *120*, 117.
(18) Cyvin, S. J.; Gutman, I. *Comput. Math. Appl.* **1986**, *12B*, 859.
(19) Gutman, I.; Cyvin, S. J. *THEOCHEM* **1986**, *138*, 325.
(20) Zhang, F. J.; Chen, R. S. *J. Nature (Chinese)* **1987**, *10*(3), 163.
(21) Cyvin, S. J.; Gutman, I. *THEOCHEM* **1988**, *164*, 183.
(22) Gutman, I.; Cyvin, S. J. *J. Serb. Chem. Soc.* **1988**, *53*, 391.
(23) Cyvin, S. J.; Gutman, I. *Kekulé Structures in Benzenoid Hydrocarbons*; Lecture Notes in Chemistry 46; Springer-Verlag: Berlin, 1988.
(24) Cyvin, S. J.; Brunvoll, J.; Cyvin, B. N. *Comput. Math. Appl.* **1989**, *17*, 355.
(25) Gutman, I.; Cyvin, S. J. *Introduction to the Theory of Benzenoid Hydrocarbons*, Springer-Verlag: Berlin, 1989.
(26) Knop, J. V.; Szymanski, K.; Jeričević, Ž.; Trinajstić, N. *J. Comput. Chem.* **1983**, *4*, 23.
(27) Knop, J. V.; Müller, W. R.; Szymanski, K.; Trinajstić, N. *Computer Generation of Certain Classes of Molecules*; Association of Chemists and Technologists of Croatia: Zagreb, 1985.
(28) Balaban, A. T.; Brunvoll, J.; Cioslowski, J.; Cyvin, B. N.; Cyvin, S. J.; Gutman, I.; He, W. C.; He, W. J.; Knop, J. V.; Kovačević, M.; Müller, W. R.; Szymanski, K.; Tošić, R.; Trinajstić, N. *Z. Naturforsch.* **1987**, *42A*, 863.
(29) He, W. J.; He, W. C.; Wang, Q. X.; Brunvoll, J.; Cyvin, S. J. *Z. Naturforsch.* **1988**, *43A*, 693.
(30) Brunvoll, J.; Cyvin, B. N.; Cyvin, S. J.; Gutman, I. *Z. Naturforsch.* **1988**, *43A*, 889.
(31) Zhang, F. J.; Guo, X. F. *MATCH* **1988**, *23*, 229.
(32) He, W. C.; He, W. J.; Cyvin, B. N.; Cyvin, S. J.; Brunvoll, J. *MATCH* **1988**, *23*, 201.
(33) Guo, X. F.; Zhang, F. J. *MATCH* **1989**, *24*, 85.
(34) Zhang, F. J.; Chen, R. S.; Guo, X. F. *Graphs Combinatorics* **1985**, *1*, 383.
(35) Kostochka, A. V. *Proc. 30th Int. Wiss. Kolloq. Tech. Hochsch. Ilmenau* **1985**, *F*, 49.
(36) He, W. C.; He, W. J. *Theor. Chim. Acta* **1985**, *68*, 301.
(37) Cyvin, S. J.; Cyvin, B. N.; Gutman, I. *Z. Naturforsch.* **1985**, *40A*, 1253.
(38) Dias, J. R. *THEOCHEM* **1986**, *137*, 9.
(39) Cyvin, S. J. *Monatsh. Chem.* **1986**, *117*, 33.
(40) Hosoya, H. *Comput. Math. Appl.* **1986**, *12B*, 271.
(41) Brunvoll, J.; Cyvin, B. N.; Cyvin, S. J. *RUN-NYTT* (Information from RUNIT, the Computer Centre at the University of Trondheim) **1986**, *13*(4), 20.

(42) Brunvoll, J.; Cyvin, B. N.; Cyvin, S. J. *J. Chem. Inf. Comput. Sci.* **1987**, *27*, 171.
(43) Cyvin, S. J.; Bergan, J. L.; Cyvin, B. N. *Acta. Chim. Hung.* **1987**, *124*, 691.
(44) Cyvin, S. J.; Brunvoll, J.; Cyvin, B. N. *MATCH* **1988**, *23*, 189.
(45) Cyvin, S. J.; Brunvoll, J.; Cyvin, B. N. *THEOCHEM* **1988**, *180*, 329.
(46) Cyvin, S. J.; Cyvin, B. N.; Brunvoll, J. *THEOCHEM* **1987**, *151*, 271.
(47) Dias, J. R. *J. Chem. Inf. Comput. Sci.* **1984**, *24*, 124.

Application of Microcomputer-Based Robust Regression Methods to Nonlinear Data Analysis

BRETT J. STANLEY and DAVID B. MARSHALL*
Department of Chemistry and Biochemistry, Utah State University, Logan, Utah 84322-0300

Received March 15, 1989

Two nonlinear robust regression methods are developed, characterized, and compared for the example case of exponential decay. Extension to other nonlinear models is obvious. The methods are computationally simple and easily programmed. The resulting programs exhibit reasonable computation times on microcomputers and are thus an easily implemented analytical tool. Programming examples of the robust regression and other methods are given for GAUSS, a particularly convenient language for algorithms that make extensive use of matrix manipulations.

INTRODUCTION

In the analysis of nonlinear data in chemistry, a common procedure is to "linearize" the data and then perform a least-squares fit. In the presence of noise this method can incur significant error because fluctuations in small numbers result in large fluctuations in the natural logs of these numbers (see Figure 1). Furthermore, this method does nothing to alleviate the effect of any outliers that may be present in the data. Robust regression, a technique for the elimination of outlying data points without the need for outlier diagnostic testing, unfortunately does not perform well on the linearized form of such data. Even more, performing data analysis on linearized data is not "correct" in that the least-squares method, which minimizes the sum square of residuals, is not minimizing the "true" model function but some other function, and the minimization itself cannot be guaranteed to have the same transform properties as the original data have.

To avoid these difficulties of analyzing transformed data, nonlinear least-squares analysis is commonly performed. This technique takes the model equation and finds the minimum on the error surface formed by the data and the model. There are many different algorithms available to find this minimum, some of which solve sets of m nonlinear equations, where m is the number of parameters in the model (such as the Gauss-Newton algorithm[1]), many of which find the minimum of a function in m variables (grid and gradient search methods,[2] simplex method,[3] etc.), and methods such as the Levenberg-Marquardt algorithm[4] compromise between downhill gradient methods and the Gauss-Newton step. Although most of these algorithms are fairly rugged in terms of resistance to initial guesses, convergence, etc., parameter estimates can be distorted by "bad" data points, or outliers, just as in the linear case. Other robust methods for nonlinear analysis have been suggested,[5] but are presently quite theoretical in nature, and the corresponding algorithms have not been fully developed or characterized yet for typical data sets that can occur in chemistry.

The nonlinear case presents a much more difficult general solution problem than that of the case of the linear problem which can be set up as the solution of a set of m simultaneous equations. Moreover, the error surfaces (χ^2, or the squared residuals) of exponential data with a corresponding function tend to possess many broad and shallow minima, sometimes making minimization tedious. For quick data analysis in the laboratory, higher level sophisticated algorithms are not applicable for routine execution on microcomputers. Reiterated least-squares solution of maximum likelihood estimators (M-estimators) represents the most general and computationally simplest approach to this problem. In this paper, two nonlinear robust estimators that are easy to program and implement into least-squares analysis routines are derived for the case of exponential data. Specifically, the M-estimators corresponding to least absolute deviations and Tukey's biweight using weighted Gauss-Newton nonlinear least-squares are developed. Extension to other model forms is straightforward. The estimators are tested with the model form in the presence of outliers and various interferences, with and without the presence of Gaussian noise. Comparisons between the two robust methods and between that of ordinary nonlinear least-squares are given, as well as the optimum conditions for the use of one estimator over that of another.

THEORY

A robust estimator is considered "robust" if it is insensitive to the effect of data points that have originated from a parent population that differs from the underlying population being analyzed. There are different types of robust estimators, a particularly common type being the M-estimators. All M-estimators follow from maximum-likelihood arguments in the same sense that least-squares estimates do and are derived as follows. First, a probability distribution to describe the data is chosen, and its maximum is found by minimizing its negative logarithm, ρ.[6] ρ is a symmetrical function of the "scaled" residuals between the data, y_i, and the model, $y(x_i;\theta)$. Minimization is performed by varying the parameter estimates θ

$$\text{minimize over } \theta \qquad \sum_{i=1}^{N} \rho(y_i - y(x_i;\theta)/\sigma_i) \qquad (1)$$

where σ is the scale and θ is the parameter estimate vector. If we then define the parameter $z \equiv [y_i - y(x_i)]/\sigma_i$, take the derivative of $\rho(z)$

$$\chi(z) \equiv \mathrm{d}\rho(z)/\mathrm{d}z \qquad (2)$$

and set it equal to zero, the generalized normal equations describing the approximate solution at the maximum are then[6]

$$0 = \sum_{i=1}^{N} 1/\sigma_i[\chi(y_i - y(x_i)/\sigma_i)(\delta y(x_i;\theta)/\delta\theta_k)] \quad k = 1, ..., m \qquad (3)$$

where m is the number of parameters in the model. In any problem, it is the normal equations that must be solved to obtain the parameter estimates, and the derivative of the model

0095-2338/89/1629-0244$01.50/0