match no. 22 pp. 175-179 1987

DISTRIBUTION OF K, THE NUMBER OF KEKULÉ STRUCTURES, IN BENZENOID HYDROCARBONS. PART IA: COMMENTS ON UPPER BOUNDS OF K

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(Received: June 1987)

Abstract: An error was detected in the derivation of one of Cyvin's inequalities for $K_{max}(h)$. New explicit formulas for upper bounds of K are presented.

INTRODUCTION AND SUMMARY OF PREVIOUS WORK

The present communication deals with upper bounds of K, the number of Kekulé structures of benzenoid systems. The results manifest themselves in inequalities for $K_{max}(h)$, where h is the number of hexagons of the benzenoids. The deductions rest on theorems which, strictly speaking, have been demonstrated for catacondensed systems only, but it has been conjectured with great confidence that the results are valid for benzenoids in general. All experience and certain (mainly empirical) considerations[1] have shown that the benzenoid with the highest K number for a given h is a catacondensed system.

The following estimate of an upper bound of K is found in the pioneering work of Gutman.[2]

$$K_{max}(h) \leq 2^{h-1} + 1 \qquad (1)$$

It is consistent with the recurrence formula:[1]

$$K_{max}(h) \leq 3K_{max}(h-1) - 2K_{max}(h-2); \qquad h \geq 3 \qquad (2)$$

Cyvin[1] produced a new recurrence formula, viz.

$$K_{max}(h) \leq K_{max}(h-1) + 2K_{max}(h-3); \qquad h \geq 4 \qquad (3)$$

This formula gives better estimates for K_{max} than (2) provided that the same initial conditions $K_{max}(1) = 2$ and $K_{max}(2) = 3$ are used in both cases, in addition to $K_{max}(3) = 5$ for eqn. (3).

The next step of Cyvin's derivation is erroneous so that eqn. (8) of Ref. 1 actually does not follow from (2) and (3) above. In consequence, also the derivation of the explicit estimate of $K_{max}(h)$ in eqn. (9) of Ref. 1 is in error.

NEW EXPLICIT ESTIMATES OF UPPER BOUNDS OF K

First approach

On combining eqn. (1) with (3) it is arrived at

$$K_{max}(h) \leq 2^{h-2} + 1 + 2(2^{h-4} + 1); \qquad h \geq 4$$

or

$$K_{max}(h) \leq 3(2^{h-3} + 1) \qquad (4)$$

which by inspection is found to be valid also for $1 \leq h < 4$. It is an explicit expression for the upper bound of K.

Second approach

In a different approach we apply

$$K_{max}(h-1) \leq 3K_{max}(h-2) - 2K_{max}(h-3); \qquad h \geq 4$$

obtained from (2). Together with (3) it yields

$$K_{max}(h) \leq 3K_{max}(h-2); \qquad h \geq 3 \qquad (5)$$

where the validity for h=3 was verified by inspection. By repeated application of this recurrence relation, together with the lowest values of K_{max}, the following explicit equations were achieved.

$$K_{max}(h) \leq \begin{cases} 3^{\frac{h}{2}}; & h = 0, 2, 4, 6, \ldots. \\ 2 \cdot 3^{\frac{h-1}{2}}; & h = 1, 3, 5, \ldots. \end{cases} \qquad (6)$$

Here we have extended the range of h to $h=0$ by means of the reasonable definition $K_{max}(0)= 1$ pertaining to the trivial case of no hexagons. The case is realized by an acyclic chain of an odd number of edges. The above equation (6), in contrast to all the other upper bound estimates, reproduces exactly this trivial K number.

Numerical results

Table 1 shows the numerical results of the three explicit upper bound estimates manifested in eqns. (1), (4) and (6).

DISCUSSION

It is seen from Table 1 that the estimate (4) is better than (1) for $h \geq 5$, but the agreement with K_{max} for the lowest h values is lost by (4). In fact the two sets obey the same re-

Table 1. Maximal K values and upper bound estimates.

h	K_{max}*	Eqn.(1)	Eqn.(4)	Eqn.(6)	Eqn.(7)	Eqn.(8)
1	2	2	3.75	2	-	2
2	3	3	4.5	3	3	3
3	5	5	6	6	5	5
4	9	9	9	9	9	9
5	14	17	15	18	15	14
6	24	33	27	27	27	24
7	41	65	51	54	45	41
8	66	129	99	81	81	66
9	110	257	195	162	135	113
10	189	513	387	243	243	189
11	(305)	1025	771	486	405	311
12	(510)	2049	1539	729	729	528
13	863	4097	3075	1458	1215	878
14	(1425)	8193	6147	2187	2187	1461
15	(2345)	16385	12291	4374	3645	2462

*From Ref. 1; parenthesized values pertain to helicene derivatives (helicenic systems).

currence relation (2), and eqn. (4) may be characterized just as a "regional improvement" as described in the previous work.[1] Many versions of such an improvement are possible. Eqn. (6), on the other hand, represents a major improvement. These estimates are found to be superior to both of the others with the exception of some cases when $h < 8$.

A slight "regional improvement" of the K_{max} estimates for odd h values, viz.

$$K_{max}(h) \leq 5 \cdot 3^{\frac{h-3}{2}}; \qquad h = 3,5,7,.... \tag{7}$$

resulted in the pertinent column of Table 1. The inequality is not valid for h=1. For all $h > 1$ one obtains either an exact fit or a better estimate than all the others which are listed here.

In general the K_{max} values are seen to be largely overestimated for high enough h values: already for h=10 the three formulas (6), (4) and (1) give the percentage deviations (from differences) equal to 29%, 105% and 171%, respectively. Therefore there is still much work left for possible improvements of these estimates.

On this background the formula of Cyvin[1] mentioned in the introductory part, has remarkable merits. It reads

$$K_{max}(h) \leq K_{max}(h-2) + 3K_{max}(h-3); \qquad h \geq 4 \tag{8}$$

With the initial conditions $K_{max}(1) = 2$, $K_{max}(2) = 3$ and $K_{max}(3) = 5$ this relation was found to reproduce exactly all K_{max} values for $h \leq 10$, except a deviation of 3% for h=9. Numerical results for $h \leq 15$ are found in the last column of Table 1. Furthermore, when including helicenic systems, all deviations for h = 1, 2, ..., 20, 22, 25 were found to be below 10%. We recall that eqn. (8) was obtained accidentally by an error in the analysis. Nevertheless it seems safe to assume that the result (8) is correct, at least with the indicated initial conditions (and probably in general). In the numerical computations described above the validity of (8) was demonstrated up to h=20, while the percentage deviation displayed a steadily increasing tendency.[1] Eqn. (8) may therefore be considered as a conjecture, which it would be worth while to attempt to prove mathematically.

REFERENCES

1. S.J. Cyvin, Match 20, 165 (1986).
2. I. Gutman, Match 13, 173 (1982).