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ESSENTIALLY DISCONNECTED BENZENOIDS: DISTRIBUTION OF K, THE NUMBER OF KEKULÉ STRUCTURES, IN BENZENOID HYDROCARBONS - VIII

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Abstract: The distribution of the number of Kekulé structures for essentially disconnected benzenoids was determined for the systems with twelve hexagons.

INTRODUCTION

An important classification of benzenoids has been termed "*neo*" [1]. The concept refers to the classes normal (n), essentially disconnected (e) and non-Kekuléan (o) benzenoids. The relevance of this classification to the Kekulé structure count has been pointed out previously [2-5].

An essentially disconnected benzenoid is defined as a Kekuléan benzenoid system with fixed bonds (single or double in all Kekulé structures). The reader should consult a recent work for a more detailed description, numerous examples, and some results of enumeration of essentially disconnected benzenoids [6].

In the computer-aided enumerations and classifications of benzenoid systems the following three principles are distinguished [7]:

(a) specific generation,
(b) recognition,
(c) exclusion.

Based on a conjecture about normal benzenoids [4] it was found possible to

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obtain these systems by specific generation. The non-Kekuléans are available by recognition. The most direct way is to compute the Kekulé structure count (K), which by definition is zero. If the grand total for the benzenoids at a given h, the number of hexagons, is known, then the number of the essentially disconnected systems is attainable by subtracting the number of normal benzenoids and of non-Kekuléans. This is an example of the principle of exclusion. It was applied in particular for the benzenoids with $h = 10$ and $h = 11$ when it was established that the respective numbers of essentially disconnected systems are 3732 and 19960 [1]. For this purpose the numbers of normal benzenoids had to be known. They were reported to be 10375 and 42919 for $h = 10$ and 11, respectively [8].

The distribution of K is defined as the numbers of benzenoids with different K numbers at a given h value. These distributions for the essentially disconnected benzenoids up to $h = 11$ have been reported previously [9]. Here again it was resorted to an indirect method by subtracting the numbers of the distribution of K for the normal benzenoids from the total.

In the present work an algorithm for recognition of essentially disconnected benzenoids is employed for the first time. Consequently these systems are obtained by a more direct method. The enumeration and the determination of the distribution of K were carried through $h = 12$.

ALGORITHM FOR RECOGNITION OF ESSENTIALLY DISCONNECTED BENZENOIDS

The following algorithm is convenient for computer programming.

The Pauling bond orders for benzenoids are known to be equal to elements of the inverse adjacency matrix [10]. An essentially disconnected benzenoid is characterized by possessing bonds with Pauling bond order equal to zero. A formulation of the necessary and sufficient condition for a benzenoid to be essentially disconnected reads:

$$(\mathrm{A})_{ij} = 1, \qquad (\mathrm{A}^{-1})_{ij} = 0$$

for at least one pair of vertices ij. Here A is the adjacency matrix.

PRACTICAL PROCEDURE

Let us shortly recapitulate the types of addition of one hexagon to the perimeter of a benzenoid. Firstly one has the three types of *normal additions*, by which the added hexagon acquires the mode [11] L_1, L_3 or L_5. These additions are also referred to as one-, three- and five-contact additions, respectively. Secondly one has the two types of *non-normal additions*, by which the added hexagon becomes P_2 or P_4. These are the two- and four-contact additions, respectively.

The invariant Δ (color excess) of a benzenoid is defined as the absolute magnitude of the difference between the numbers of black and white vertices. The *selection rules* for Δ may be formulated as: (1) by a normal addition the Δ value of the benzenoid is unchanged; (2) by a non-normal addition the Δ value changes by ± 1 [12].

After these preparations we are able to sketch the procedure actually used in the computer-programming.

Assume that a data base for all the 30086 benzenoids with $h = 10$ classified according to the Δ values is available. This distribution counts 14107, 14024, 1916 and 39 systems for $\Delta = 0$, 1, 2 and 3, respectively [1]. We are interested in generating the benzenoid systems with $\Delta = 0$ for $h = 11$ and 12, since we know that all essentially disconnected benzenoids have $\Delta = 0$. When this is done, the algorithm described above may be applied in order to recognize and enumerate the essentially disconnected benzenoids among the generated systems. It is not necessary to eliminate duplicated (isomorphic) systems before the algorithm of recognition has been executed. This fact may save computer time since the checking for non-isomorphy usually is a relatively time-consuming process.

In order to generate the benzenoids with $h = 11$, $\Delta = 0$ it is sufficient to apply normal additions to all systems with $h = 10$, $\Delta = 0$ and non-normal additions to all systems with $h = 10$, $\Delta = 1$; cf. Fig. 1. In the last part of this process (non-normal additions) also some systems with $h = 11$, $\Delta = 2$ are generated (cf. a dotted arrow in Fig. 1); they may easily be recognized and eliminated successively.

In the same way we generated the systems with $h = 12$, $\Delta = 0$ from the systems with $h = 11$, $\Delta = 0$ and $h = 11$, $\Delta = 1$. The latter set was generated from the data base for $h = 10$ as indicated in Fig. 1, all the time employing the selection rules for Δ.

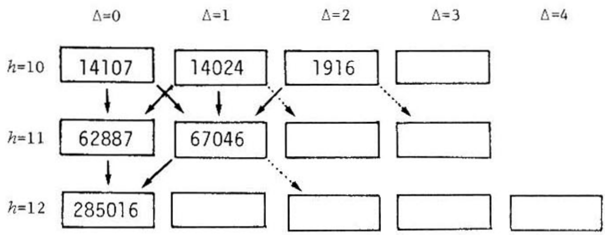

Fig. 1. Schematic representation of the generation of the benzenoid systems with $h = 12$, $\Delta = 0$, starting with a data base for $h = 10$. Numbers of benzenoids for the relevant h and Δ values are specified.

RESULTS OF ENUMERATION

The deduced numbers of essentially disconnected benzenoids for $h = 10$ and $h = 11$ reproduced exactly the previous results [1]; cf. also the INTRODUCTION. Also the distributions into symmetry groups coincide with the previous findings [6]. In Table 1 we give these data along with the new results for $h = 12$.

Table 1. Numbers of essentially disconnected benzenoids for $h = 10$, 11 and 12, classified according to symmetry.

h	D_{2h}	C_{2h}	C_{2v}	C_s	Total
10	1	53	31	3647	3732
11	2	87	166	19705	19960
12	5	306	202	104200	104713

DISTRIBUTION OF K

The Kekulé structure counts, K, were computed for the generated essentially disconnected systems. The distribution of K refers to the numbers of systems with the different K values at a given h. It is gratifying that the distributions of K at $h = 10$ and $h = 11$ published recently [9] were reproduced exactly. In the previous work [9] these numbers were obtained more indirectly by subtractions; cf. the INTRODUCTION.

Table 2 gives a full account of the distribution of K for essentially disconnected benzenoids with $h = 12$ deduced in the present work.

AVERAGE K VALUES AND RELATED QUANTITIES, $(\ln\langle K\rangle)/h$

From the present analysis we found for the essentially disconnected benzenoids with $h = 12$:

$$\langle K\rangle = 119.34, \qquad (\ln\langle K\rangle)/h = 0.3985$$

These values supplement the data of previous publications [3, 8, 9].

Figure 2 shows a diagram of the quantities under consideration, $(\ln\langle K\rangle)/h$, as a function of h. The anomaly from $h = 10$ to $h = 11$, where the curve ascends, was already pointed out previously [9]. We find again a "normal" behaviour from $h = 11$ to $h = 12$, viz. a descending curve.

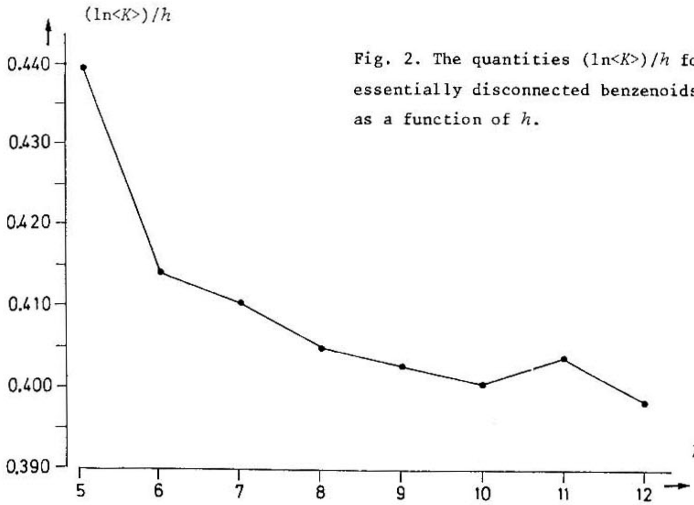

Fig. 2. The quantities $(\ln\langle K\rangle)/h$ for essentially disconnected benzenoids as a function of h.

Table 2. Numbers of essentially disconnected benzenoids, N, for given K values at h = 12.

K	N	K	N	K	N	K	N
9	706	93	503	169	225	242	102
12	874	95	581	170	471	243	181
15	1169	96	1027	171	919	244	9
16	302	98	382	172	216	245	298
18	778	99	1206	174	435	246	231
20	750	100	632	175	627	247	276
21	949	102	606	176	498	248	252
24	1212	104	596	177	394	249	136
25	527	105	1400	180	1080	250	204
27	1124	108	1284	182	499	252	361
28	611	110	542	183	369	253	53
30	1084	111	429	184	524	255	186
32	473	112	697	185	318	256	70
33	800	114	562	186	420	258	152
35	819	115	517	187	293	259	36
36	1611	116	322	188	187	260	150
39	696	117	1099	189	818	261	105
40	880	119	460	190	258	264	218
42	1021	120	1557	192	741	265	85
44	511	121	319	195	774	266	56
45	1730	123	514	196	343	267	161
48	1182	124	371	198	808	270	144
49	360	125	434	200	653	272	179
50	358	126	1244	201	310	273	171
51	529	128	408	203	345	275	123
52	450	129	464	204	510	276	123
54	1000	130	507	205	365	279	36
55	704	132	1023	207	405	280	108
56	807	133	501	208	405	282	78
57	602	135	1190	209	344	285	126
60	1565	136	588	210	642	286	81
63	1430	138	499	212	69	288	119
64	453	140	681	213	367	290	67
65	624	141	437	215	250	291	33
66	732	143	515	216	582	294	53
68	342	144	1150	217	342	295	44
69	507	145	460	219	257	296	25
70	721	147	924	220	371	297	11
72	1514	148	275	221	234	299	41
75	1105	150	936	222	230	300	64
76	404	152	475	224	215	303	7
77	613	153	844	225	297	304	10
78	658	154	602	228	449	305	10
80	769	155	520	230	233	306	10
81	895	156	976	231	396	308	12
84	1283	159	426	232	308	310	12
85	502	160	570	234	418	312	3
87	481	161	466	235	216	315	9
88	596	162	771	236	39	318	1
90	1359	164	325	237	317	320	6
91	561	165	1013	238	300	321	1
92	354	168	1140	240	535	322	6

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