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THE NUMBER OF PYRENE ISOMERS IS STILL UNKNOWN

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Abstract: The number of $C_{16}H_{10}$ isomers of polycyclic conjugated hydrocarbons with two internal vertices is determined to be 91. These isomers include pyrene. The systems are classified according to symmetry.

The benzenoid (conjugated) hydrocarbons have been studied to a large extent with respect to their chemical formulas, C_nH_s, and the C_nH_s isomers [1,2]. But it is also of interest to investigate nonbenzenoid conjugated hydrocarbons with C_nH_s formulas, which also have benzenoid isomers [3]. An instructive introduction to this problem is the inspection of the $C_{16}H_{10}$ isomers. Pyrene is the only benzenoid hydrocarbon with this formula.

Class of hydrocarbons. In order to define the problem precisely it is important to specify the class of hydrocarbons which is to be taken into account. We shall consider the systems (molecular graphs) which consist of simply connected polygons, where any two polygons either share exactly one edge or they are disjoint. In consequence, only vertices of degrees two and three will be present. These systems correspond to polycyclic conjugated hydrocarbons. In the C_nH_s formula, the number of carbon atoms (n) corresponds to the number of vertices, while the number of hydrogens (s) corresponds to the number of vertices of degree two.

Notation. Let the number of polygons in a system, corresponding to the number of rings in a hydrocarbon, be denoted by r. The rings may in general be q–membered, where $q \geq 3$. Correspondingly, we shall speak about q–gons. Denote the number of q–gons by r_q.

Then

$$r = \sum_{q=3}^{q_{max}} r_q \tag{1}$$

Let Σq be defined as the sum of the numbers of edges for all the polygons taken individually, viz.

$$\Sigma q = \sum_{q=3}^{q_{max}} q r_q \tag{2}$$

Another important quantity is the number of internal vertices, say n_i. An internal vertex is by definition shared among three polygons.

Fundamental relations. The number of polygons (r) is given in terms of the formula coefficients (of C_nH_s) by

$$r = \tfrac{1}{2}(n - s) + 1 \tag{3}$$

independently of the sizes of the polygons, viz. the values of q.

For the quantity Σq of eqn. (2) it is easily found:

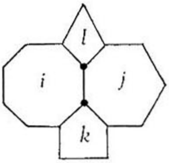
$$\Sigma q = n + 2r + n_i - 2 \tag{4}$$

Application to pyrene isomers. The fundamental relations (3) and (4) lead to very simple combinatorial principles for the deduction of the $C_{16}H_{10}$ (pyrene) isomers. Firstly, eqn. (3) gives $r = 4$; in other words, anyone of the isomers holds four rings. Secondly, four polygons can only be combined, within the present restrictions, so that $n_i = 0$, 1 or 2. For these three cases, eqn. (4) gives $\Sigma q = 22$, 23 and 24, respectively.

Pyrene isomers with two internal vertices.

Generation and enumeration. In the following we shall deduce all the $C_{16}H_{10}$ isomers within the defined class of hydrocarbons for $n_i = 2$.

The systems under consideration must have a structure like:



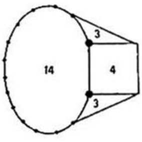
$(i,j)(k,l)$

Here the internal vertices are marked by black dots. In the coding (see above) the first pair, (i,j), refers to the q–values for the two polygons which share the two internal vertices; the second pair, (k,l), pertains to the two disjoint polygons. One has:

$$\Sigma q = i + j + k + l = 24 \qquad (5)$$

In the above example, $i = 8$, $j = 7$, $k = 5$, $l = 4$. Now one only has to take all combinations of the integers i, j, k, $l \geq 3$ which add up to 24 under the restrictions: (a) interchanging of two numerals of the same pair (in parentheses) is not allowed; (b) the numeral 3 must not occur in the first pair. The violation of (a) leads to isomorphic systems; here it is convenient to introduce the convention $i \geq j$, $k \geq l$. If $i = 3$ or $j = 3$, i.e. when the condition (b) is violated, then it is not possible to construct an appropriate system.

The largest possible polygon size (q value) is obviously 14 in the code (14,4)(3,3).



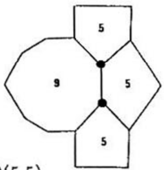
(14,4)(3,3)

The second pair (3,3) can be combined with the first pairs: (14,4), (13,5), (12,6), (11,7), (10,8), (9,9). Here $k + l = 6$, the smallest possible value. In the next step, let $k + l = 7$, which corresponds to (4,3) as the second pair. This pair can be combined with five different first pairs. Proceed successively to increase $k + l$ by unity; for $k + l = 8$ one has two possible second pairs, viz. (5,3) or (4,4); each of them can be combined with five different first pairs, etc. The result of this enumeration is summarized below.

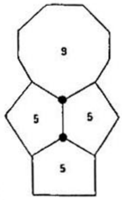
$k+l$	# first pairs	# second pairs	# isomers
6	6	1	6
7	5	1	5
8	5	2	10
9	4	2	8
10	4	3	12
11	3	3	9
12	3	4	12
13	2	4	8
14	2	5	10
15	1	5	5
16	1	6	6

In total: 91 isomers. The symmetric patterns in the above table are apparent.

Examples. There are exactly five among the considered isomers where three and only three polygons have equal size: (12,4)(4,4), (7,7)(7,3), (9,5)(5,5), (5,5)(9,5), (4,4)(12,4). Two of these systems are depicted below.



(9,5)(5,5)



(5,5)(9,5)

A unique isomer exists for all the four polygons equal: (6,6)(6,6), viz. pyrene.

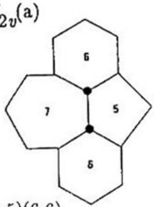
Symmetry. Three symmetry groups are possible for the systems under consideration: D_{2h}, C_{2v} and C_s. Furthermore, we shall distinguish between the two types: C_{2v}(a) where the two–fold symmetry axis (C_2) intersects the edge between the two internal vertices perpendicularly; C_{2v}(b) where C_2 goes through the two internal vertices. These symmetries are distinguished in the following way. D_{2h}: $i = j$ & $k = l$; C_{2v}(a): $i \neq j$ & $k = l$; C_{2v}(b) : $i = j$ & $k \neq l$; C_s: $i \neq j$ & $k \neq l$.

The generated systems were classified according to symmetry with the result:

Symmetry	# isomers
D_{2h}	6
C_{2v}(a)	15
C_{2v}(b)	15
C_s	55

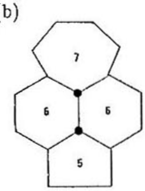
Examples.

C_{2v}(a)



(7,5)(6,6)

C_{2v}(b)



(6,6)(7,5)

Computerization. A computer program was written in order to check the above results. Sets of i, j, k, l numbers were produced by brute force, whereafter forbidden combinations and combinations which would generate isomorphic systems were eliminated. The output matched perfectly the present analytical results.

Conclusion. The present problem of the number and forms of $C_{16}H_{10}$ isomers was posed by Dias [4] in this journal, but he did not give a satisfactory solution. Dias [3,4] claimed that there are 420 appropriate isomers with ring sizes up to nine ($q \leq 9$). Among his depictions there are 38 such systems with $n_i = 2$, while the present result (for $q \leq 9$) is 56.

It remains to derive the correct numbers of $C_{16}H_{10}$ isomers for the systems with $n_i = 1$ and $n_i = 0$. Also in these cases the fundamental relations (3) and (4) are supposed to be useful, but more complications are expected than in the case of $n_i = 2$.

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References

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[2] J. Brunvoll, B. N. Cyvin and S. J. Cyvin, Topics in Current Chemistry *162*, 181 (1992).

[3] J. R. Dias, Handbook of Polycyclic Hydrocarbons, Part B, Elsevier, Amsterdam 1988.

[4] J. R. Dias, Match *14*, 83 (1983).