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Numbers of Isomers of Some Classes of Pentacyclic Conjugated Hydrocarbons

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The pentacyclic structures are considered within the initiated studies of polycyclic conjugated hydrocarbons. A complete mathematical solution (in terms of generating functions) is presented for the numbers of C_nH_s isomers of these structures. Some details of the analysis are given for the doubly-branched catafused structures of the category in question, a subclass to which $C_{16}H_8$ cyclic bicalicene and $C_{24}H_{16}$ tetraphenylene belong.

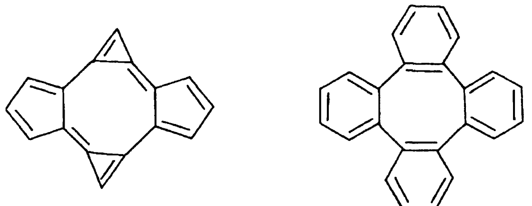
This work was inspired by Aihara,[1] who performed some theoretical studies on $C_{16}H_8$ cyclic bicalicene (Fig. 1)[2,3] and one of its isomers. Here we give the total number of isomers for a subclass of hydrocarbons to which cyclic bicalicene belongs. This finding is put into a broader context by considering rather general classes of pentacyclic conjugated hydrocarbons.

Two previous papers[4,5] represent a modest start of systematic enumerations of isomers of polycyclic conjugated hydrocarbons. Therein the enumeration problems were only solved for $r \leq 3$ and partly for $r=4$, where r is used to designate the number of rings. In cyclic bicalicene, $r=5$.

Definitions

The polycyclic conjugated hydrocarbons which are considered here, should be completely fused in the sense that every carbon–carbon bond should belong to at least one ring. More precisely, the class of interest is defined in terms of chemical graphs[6] as represented by polygonal systems P. A system P consists 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 are present, and those of degree two are only found on the perimeter (outer boundary). A formula C_nH_s is associated with P, as well as the corresponding hydrocarbon. Here the number of carbon atoms (n) corresponds to the total number of vertices in P, while the number of hydrogens (s) corresponds to the number of vertices of degree two. The number of C_nH_s isomers for a class of polycyclic conjugated hydrocarbons is defined as the number of nonisomorphic polygonal systems which correspond to this class. The symmetry group of an isomer is defined in relation to the corresponding geometrically planar polygonal system with the highest possible symmetry.

A polygonal system P is said to be catafused when it does not possess any internal vertex (shared by three polygons); otherwise P is perifused. The number of polygons in P is r.



$C_{16}H_8$ $C_{24}H_{16}$

Fig. 1. Cyclic bicalicene ($C_{10}H_8$) and tetraphenylene ($C_{24}H_{16}$).

Pentacyclic Conjugated Hydrocarbons

From well-known graph theoretical properties it is easily obtained

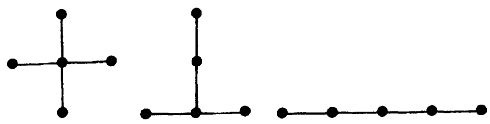
$$r = \frac{1}{2}(n-s)+1. \tag{1}$$

Therefore the formula of a pentacyclic ($r=5$) conjugated hydrocarbon has the form $C_{s+8}H_s$.

Among the catafused $r=5$ systems P three subclasses are distinguished, which presently shall be referred to as doubly-branched (db), branched (br) and unbranched (ub). They are characterized by three different inner duals;[6,7] see Fig. 2. Cyclic bicalicene[1—3] is a doubly-branched catafused pentacyclic conjugated hydrocarbon. Correspondingly, eleven subclasses of perifused $r=5$ systems P were identified in terms of different inner duals. For the sake of brevity they are not reproduced here.

Isomers of Doubly-Branched Catafused Pentacyclic Conjugated Hydrocarbons

A structure belonging to the title subclass may have the symmetry D_{4h}, D_{2h}, C_{2h}, C_{2v}, or C_s. The C_nH_s isomers of the symmetrical structures (for all symmetry groups different from C_s) were enumerated by combinatorial techniques not needed to be detailed here. It is convenient to express the results by generating functions, which has been done many times before in enumeration problems.[8—11] Here the pertinent generating functions are identified by the symbols S, D, C, M, and U for the five symmetry groups in the same order as



(db) (br) (ub)

Fig. 2. Inner duals for the doubly-branched (db), branched (br), and unbranched (ub) catafused polygonal $r=5$ systems.

they are given above. It was found:

$$S(x) = x^4(1-x^4)^{-2} = x^4 + 2x^8 + \cdots, \quad (2)$$

$$D(x) = 2x^6(1-x^2)^{-1}(1-x^4)^{-2} = 2x^6 + 2x^8 + 6x^{10} + \cdots, \quad (3)$$

$$C(x) = x^8(1-x^2)^{-2}(1-x^4)^{-2} = x^8 + 2x^{10} + \cdots, \quad (4)$$

$$M(x) = 2x^5(1-x)^{-2}(1-x^2)^{-2}(1-x^4)^{-1} = 2x^5 + 4x^6 + 10x^7 + 16x^8 + 30x^9 + 44x^{10} + \cdots. \quad (5)$$

The functions (2) — (5) (Eqs. 2, 3, 4, and 5) generate the appropriate numbers of $C_{s+8}H_s$ isomers on expansion in powers of s, i.e. as coefficients of x^s. The symmetry has also been exploited many times before in enumeration problems.[8—14] In the present case it was found that the generating function

$$J(x) = \sum_{s=4}^{\infty} \binom{s+3}{7} x^s = x^4(1-x)^{-8} \quad (6)$$

reproduces numbers which count the D_{4h} isomers once, the D_{2h} isomers twice, the C_{2h} and C_{2v} isomers four times each, and finally the C_s isomers eight times. Accordingly,

$$J(x) = S(x) + 2D(x) + 4C(x) + 4M(x) + 8U(x). \quad (7)$$

The number of distinct isomers is reproduced by

$$I(x) = S(x) + D(x) + C(x) + M(x) + U(x). \quad (8)$$

On eliminating $U(x)$ from Eqs. 7 and 8 and combination with Eqs. 2, 3, 4, 5, and 6 one arrives at the explicit form of the generating function of the numbers of $C_{s+8}H_s$ isomers for the title structures;

$$I(x) = \frac{x^4(1-2x+4x^2+x^4+2x^5+2x^6)}{(1-x)^4(1-x^2)^2(1-x^4)^2} = x^4 + 2x^5 + 8x^6 + 20x^7 + 53x^8 + 114x^9 + 242x^{10} + \cdots. \quad (9)$$

From the above analysis it is inferred that the number of $C_{16}H_8$ isomers is 53 for the doubly-branched catafused pentacyclic conjugated hydrocarbons (including cyclic bicalicene). These isomers are distributed as 8+10+17+10+8 for ring sizes of the central ring equal to 12, 11, 10, 9, and 8, respectively. Their distribution into symmetry groups is given by $2D_{4h}+2D_{2h}+C_{2h}+16C_{2v}+32C_s$ in consistency with Eqs. 2, 3, 4, and 5. The forms are depicted in Fig. 3.

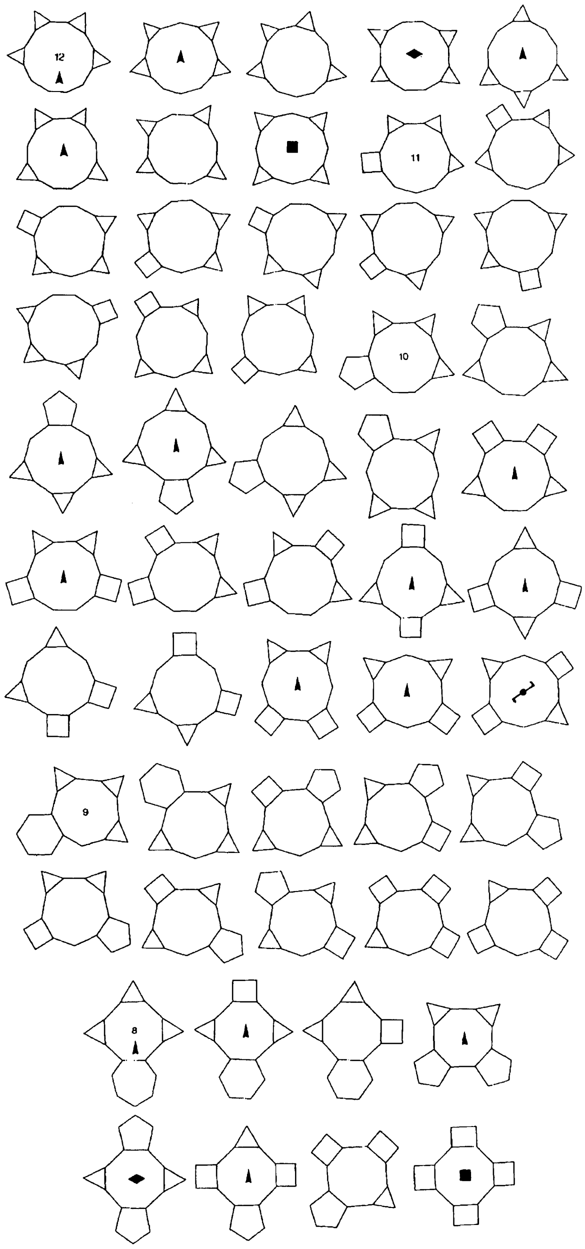


Fig. 3. The 53 $C_{16}H_8$ isomers of doubly-branched catafused pentacyclic conjugated hydrocarbons. Symmetry groups are indicated with self-explanatory symbols for D_{4h}, D_{2h}, C_{2h}, and C_{2v}. Unmarked structures belong to C_s. Inscribed numerals indicate the sizes of the central rings.

Isomers of Catafused Pentacyclic Conjugated Hydrocarbons

The branched (br) and unbranched (ub) systems (cf. Fig. 2) were analyzed in the same way as the doubly-branched (db) systems. When adding the contributions from these three subclasses one arrives at the numbers of isomers for the title class of hydrocarbons. The following generating function for these numbers was derived:

$$I_5^{\mathrm{cata}}(x) = \frac{x^2(1+7x^2+2x^3+16x^4+8x^5+11x^6+6x^7+5x^8)}{(1-x)^4(1-x^2)^2(1-x^4)^2} = x^2 + 4x^3 + 19x^4 + 58x^5 + 168x^6 + 408x^7 + 923x^8 + 1890x^9 + 3663x^{10} + \cdots. \quad (10)$$

Isomers of Pentacyclic Conjugated Hydrocarbons

Also the eleven subclasses of perifused $r=5$ systems (see above) were analyzed with respect to the numbers of isomers. On adding the contributions from these subclasses it was arrived at:

$$I_5^{\text{peri}}(x) = \frac{5-5x+8x^2+5x^3+3x^4+5x^5+6x^6-5x^7+2x^8}{(1-x)^4(1-x^2)^2(1-x^4)}. \quad (11)$$

Hereby the enumeration problem for the C_nH_s isomers of a rather general class of hydrocarbons is solved; on adding Eqs. 10 and 11 one obtains the numbers for all pentacyclic conjugated hydrocarbons (within the specified category). There is no limit upwards for the ring sizes (≥ 3). The generating function for this grand total, viz. I_5, yields:

$$\begin{aligned} I_5(x) &= I_5^{\text{cata}}(x) + I_5^{\text{peri}}(x) \\ &= 5+15x+49x^2+121x^3+293x^4+624x^5+1282x^6 \\ &\quad +2442x^7+4484x^8+7815x^9+13197x^{10}+\cdots . \end{aligned} \quad (12)$$

Accordingly, there are 4484 $C_{16}H_8$ isomers of polycyclic conjugated hydrocarbons in total.

Another Example

$C_{24}H_{16}$ tetraphenylene (Fig. 1) is a classical compound[15] within the category of doubly-branched polycyclic conjugated hydrocarbons. For this formula ($C_{24}H_{16}$) we find, on expansions of the functions (9), (10), and (12) (Eqs. 9, 10, and 12), the numbers of isomers 6478, 74818, and 166967, respectively.

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