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# MOMENTS AND CHARACTERISTIC POLYNOMIALS OF BIPARTITE HÜCKEL GRAPHS

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## Abstract

Moments ($u_k$) and coefficients of characteristic polynomials ($a_k$) have been evaluated in terms of molecular fragments up to $k = 12$ for bipartite Hückel graphs. Based on combinatorial analysis, each coefficient can be derived as a combination of binomial factors mapping to the corresponding multi-component graphs. The general formula becomes lengthy as $k$ increases, but can be considerably simplified for a homologous series. This has been illustrated by dealing with the cata-condensed benzenoid hydrocarbons as a corollary where a rather compact set of $a_k$ has been deduced. On combining the present result with Coulson's formula, one gains insight into the relative stability of isomers in relationship to the energy contribution of fragments classified as stabilized and destabilized species.

## 1. Introduction

The evaluation of characteristic polynomials is currently carried out either by expanding the determinant defined or by directly computing the coefficients involved [1 – 14]. Little has been published on the relationship between characteristic polynomials and molecular fragments, which seems fundamentally important for interpreting molecular behaviour in terms of local structures [15]. Recently, moment analysis has been used as a tool because moments connect with molecular fragments on the one hand, and with some graph invariants on the other hand [14,15]. The importance of moments and fragments in chemical graph theory is based on the fact that they can be used as variables for characterizing the local topology of a graph [14 – 18]. Topics related to acyclic hydrocarbons were always concentrated on the total electron energy and coefficients of characteristic polynomials which have been extended to cyclic systems [15].

In this paper, moments ($u_k$) and coefficients of characteristic polynomials ($a_k$) are evaluated up to $k = 12$ for bipartite Hückel graphs. The general formulas expressed in terms of fragments become lengthy when $k$ becomes large. However, if one confines oneself to a homologous series, the situation becomes more simplified because independent fragments are greatly diminished. As an illustration, moments and $a_k$'s of cata-condensed benzenoid hydrocarbons have been deduced and formulated in terms of graph variables, introduced by Balaban [18]. In combination with Coulson's formula, one obtains insight into the role played by various fragments which can be reasonably classified as stabilized and destabilized species. A qualitative scheme for interpreting the relative stability of cata-condensed benzenoid hydrocarbon isomers is proposed on the basis of comparing the energy contribution by counting fragments.

## 2. Moments and molecular fragments

Because there are no non-zero odd moments for alternants, we concentrate on even moments. Obviously, each moment for any molecule can be partitioned additively into acyclic and cyclic components ($u'_{2l}$ and $u''_{2l}$) [15]:

$$u_{2l} = u'_{2l} + u''_{2l} , \tag{1}$$

with

$$u'_{2l} = \sum_{G'} C_{2l}^{G'}[G'] \tag{2}$$

$$u''_{2l} = \sum_{G''} C_{2l}^{G''}[G''] , \tag{3}$$

where $[G']$ or $[G'']$ represents the number of acyclic fragment $G'$ or of cyclic fragment $G''$ involved in the molecule. $C_{2l}^{G'}$ ($C_{2l}^{G''}$) enumerates the self-adjoint walks of length $2l$ spanned by $G'$ ($G''$). Equation (2) has been discussed in detail [16], so we put emphasis on eq. (3) after briefly reviewing various acyclic fragments $G'$ used in eq. (2).

The acyclic fragments with $l$ less than 6 are listed in fig. 1, where the symbol $[N' - n, a, b, \ldots, n - a - b - \ldots]$ signifies the topology of $G'$ composed of $N'$ points, $N' - n$ represents the length of the main chain, and $a, b, \ldots$ stands for the lengths of first, second, ..., straight side chains, respectively.

In order to formulate eq. (3) up to $l = 6$, sixty-five cyclic fragments are listed in fig. 2, where brackets are used for the same purpose to characterize $G''$.

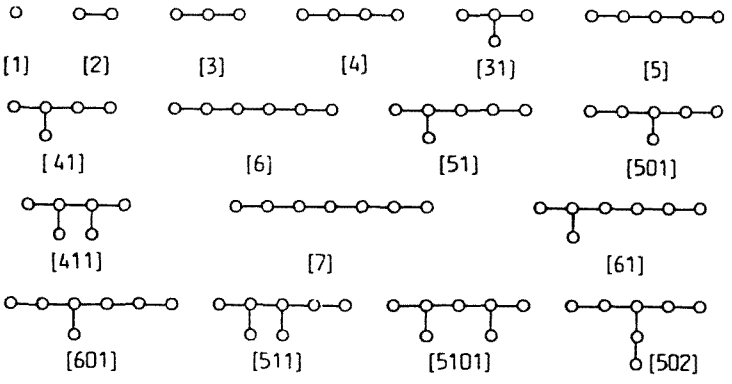



Fig. 1. Acyclic fragments for $l \leqslant 6$.

The symbol $[\overline{n}, a^{\alpha}, b^{\beta}, \ldots]$ signifies the topology of a mono-cyclic fragment in which an $n$-membered ring is linked to side chains $a, b, \ldots$ at their sites $\alpha, \beta, \ldots$, respectively. As a rule, these site symbols $\alpha, \beta, \ldots$ are omitted in cases of shortest chains [1] and [2]. For double cyclic structures, the coupled bracket $[\overline{n}, a^{\alpha}, b^{\beta}, \ldots | \overline{m}, c^{\gamma}, d^{\delta}, \ldots]$ is adopted if a common edge is shared by $n$- and $m$-membered rings simultaneously. On the other hand, the symbol $[\overline{n}, a^{\alpha}, b^{\beta}, \ldots -\overline{m}, c^{\gamma}, d^{\delta}, \ldots]$ is used if the rings connect via another edge. The side chains $a, b, \ldots$ and $c, d, \ldots$ belonging to the $n$- and $m$-membered rings, respectively, are arranged in order with respect to the shared or connected edge. For multi-cyclic species, it is straightforward to generalize this symbology.

With the specification of $G''$ in fig. 2, equation (3) can be derived one by one after the coefficient $C_{2l}^{G''}$ has been carried out. We list $u''_{2l}$, with $l$ up to 6, in the following:

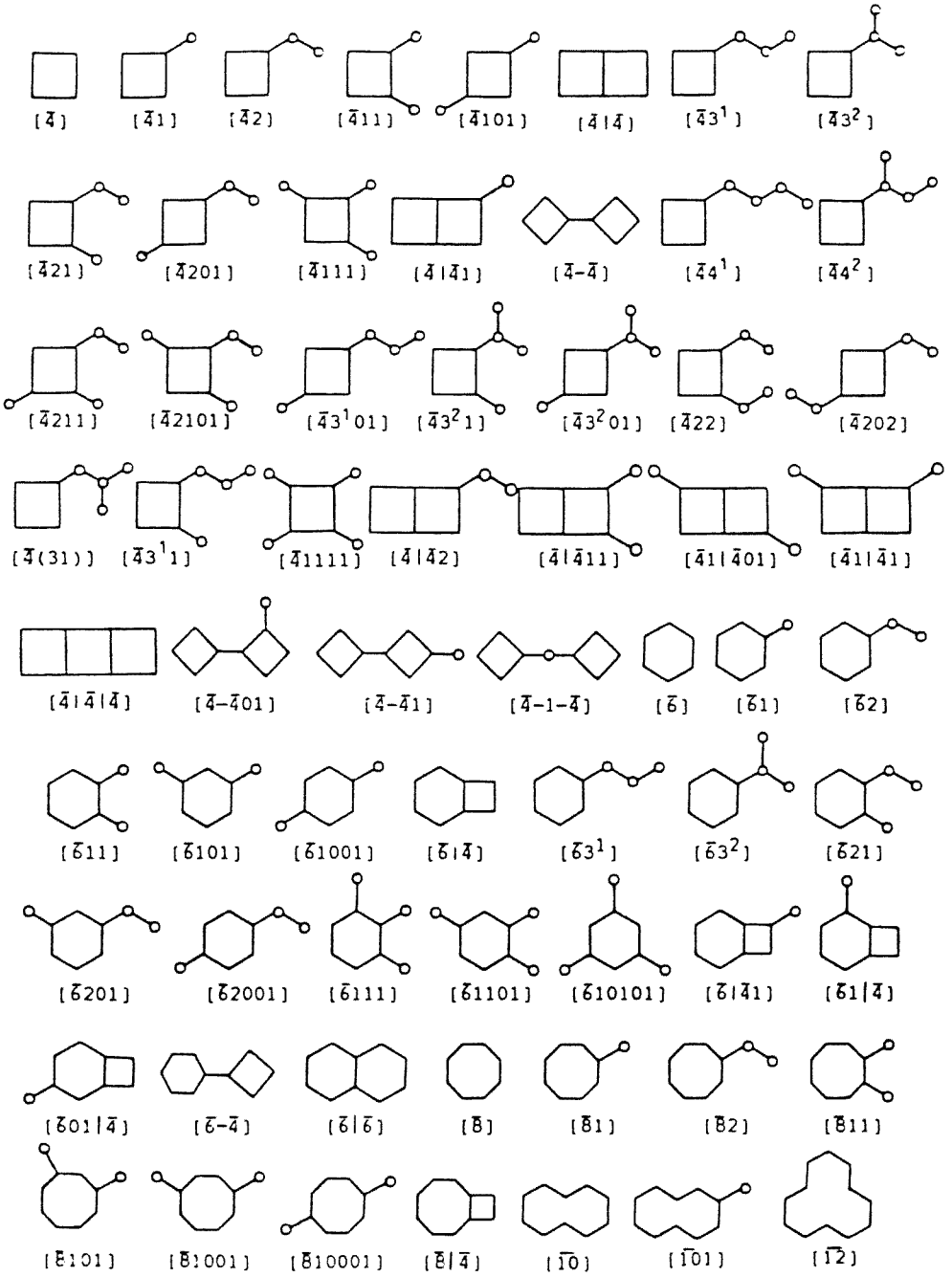



Fig. 2. Diagrams and symbols of cyclic fragments when $l \leqslant 6$.

$$u_2'' = 0$$

$$u_4'' = 8[\bar{4}]$$

$$u_6'' = 48[\bar{4}] + 12[\bar{4}1] + 12[\bar{6}]$$

$$\begin{aligned} u_8'' = {} & 264[\bar{4}] + 112[\bar{4}1] + 96[\bar{6}] + 16[\bar{4}2] + 16[\bar{4}11] \\ & + 16[\bar{4}101] + 48[\bar{4}|\bar{4}] + 16[\bar{6}1] + 16[\bar{8}] \end{aligned}$$

$$\begin{aligned} u_{10}'' = {} & 1320[\bar{4}] + 840[\bar{4}1] + 540[\bar{6}] + 180[\bar{4}2] + 220[\bar{4}11] + 200[\bar{4}101] \\ & + 900[\bar{4}|\bar{4}] + 180[\bar{6}1] + 160[\bar{8}] + 20[\bar{4}3^1] + 40[\bar{4}3^2] \\ & + 20[\bar{4}21] + 20[\bar{4}201] + 20[\bar{4}111] + 60[\bar{4}|\bar{4}1] + 40[\bar{4}-\bar{4}] \\ & + 20[\bar{6}2] + 20[\bar{6}11] + 20[\bar{6}101] + 20[\bar{6}1001] + 60[\bar{6}|\bar{4}] \\ & + 20[\bar{8}1] + 20[\bar{10}] \end{aligned}$$

$$\begin{aligned} u_{12}'' = {} & 6128[\bar{4}] + 5508[\bar{4}1] + 2724[\bar{6}] + 1448[\bar{4}2] + 2232[\bar{4}11] \\ & + 1944[\bar{4}101] + 10032[\bar{4}|\bar{4}] + 1344[\bar{6}1] + 1508[\bar{8}] \\ & + 264[\bar{4}3^1] + 576[\bar{4}3^2] + 312[\bar{4}21] + 288[\bar{4}201] \\ & + 360[\bar{4}111] + 1512[\bar{4}|\bar{4}1] + 672[\bar{4}-\bar{4}] + 264[\bar{6}2] \\ & + 312[\bar{6}11] + 288[\bar{6}101] + 288[\bar{6}1001] + 1104[\bar{6}|\bar{4}] \\ & + 264[\bar{8}1] + 240[\bar{10}] + 24[\bar{4}4^1] + 48[\bar{4}4^2] + 48[\bar{4}(31)] \\ & + 24[\bar{4}3^1 1] + 24[\bar{4}3^1 01] + 48[\bar{4}3^2 1] + 48[\bar{4}3^2 01] \\ & + 24[\bar{4}22] + 24[\bar{4}202] + 24[\bar{4}211] + 24[\bar{4}2101] \\ & + 24[\bar{4}1111] + 72[\bar{4}|\bar{4}2] + 72[\bar{4}|\bar{4}11] + 72[\bar{4}1|\bar{4}1] \\ & + 72[\bar{4}1|\bar{4}01] + 408[\bar{4}|\bar{4}|\bar{4}] + 48[\bar{4}-\bar{4}1] + 48[\bar{4}-\bar{4}01] \\ & + 48[\bar{4}-1-\bar{4}] + 24[\bar{6}3^1] + 48[\bar{6}3^2] + 24[\bar{6}21] \\ & + 24[\bar{6}201] + 24[\bar{6}2001] + 24[\bar{6}111] + 24[\bar{6}1101] \\ & + 24[\bar{6}10101] + 72[\bar{6}|\bar{4}1] + 72[\bar{6}1|\bar{4}] + 72[\bar{6}01|\bar{4}] \\ & + 72[\bar{6}|\bar{6}] + 48[\bar{6}-\bar{4}] + 24[\bar{8}2] + 24[\bar{8}11] + 24[\bar{8}1001] \\ & + 24[\bar{8}1001] + 24[\bar{8}10001] + 72[\bar{8}|\bar{4}] + 24[\bar{10}1] + 24[\bar{12}]. \end{aligned} \quad (4)$$

## 3. Coefficients of the characteristic polynomial

For any bipartite graph, the characteristic polynomial is typically as follows:

$$P_G(x) = x^N + a_2 x^{N-2} + a_4 x^{N-4} + \ldots + a_{2l} x^{N-2l} + \ldots + a_N \tag{5}$$

and the coefficient $a_k$ is related to moments that fulfill [14]:

$$a_k = \sum_{m_1, m_2, \ldots, m_k} \prod_{l=1}^{k} \frac{1}{m_l!} \left(-\frac{u_l}{l}\right)^{m_l}, \tag{6}$$

where $m_1, m_2, \ldots, m_k$ represent a numerical set of $k$ integers satisfying

$$1m_1 + 2m_2 + \ldots + km_k = k\,. \tag{7}$$

Substituting the results of eqs. (2) and (3) into eq. (6), one readily obtains the following formulas in terms of molecular fragments:

$$\begin{aligned}
a_2 &= -[2] \\
a_4 &= 2^{-1}([2]^2 - [2] - 2[3]) - 2[4] \\
a_6 &= -6^{-1}([2]^3 - [2]^2 + 6[2][3] + 2[2] + 12[3] + 6[4] + 12[31]) \\
&\quad + 2[\bar{4}][2] - 8[\bar{4}] - 2[\bar{4}1] - 2[\bar{6}] \\
a_8 &= 24^{-1}([2]^4 - [2]^3 - 12[2]^2[3] + 11[2]^2 + 60[2][3] + 24[2][4] + 48[2][31] \\
&\quad - 6[2] + 12[3]^2 - 84[3] - 96[4] - 216[31] - 24[5] - 48[41]) \\
&\quad + 2[\bar{4}]^2 - [\bar{4}][2]^2 + 9[\bar{4}][2] + 2[\bar{4}][3] - 33[\bar{4}] + 2[\bar{4}1][2] \\
&\quad - 14[\bar{4}1] + 2[\bar{6}][2] - 12[\bar{6}] - 2[\bar{4}2] - 2[\bar{4}11] - 2[\bar{4}101] \\
&\quad - 6[\bar{4}|\bar{4}] - 2[\bar{6}1] - 2[\bar{8}] \\
&\ldots
\end{aligned} \tag{8}$$

However, the formula becomes complicated and irregular when $k \geqslant 10$. By means of combinatorial analysis (see ref. [14]), it is possible to transform each member of eq. (8) into a combination of binomial factors mapping one to one with a set of graphs. As usual, these graphs are multi-component, satisfying

$$p + 2q = k\,, \tag{9}$$

where $p$ is the number of ring edges (or points) and $q$ is the number of chain edges. For example, we have $p = 4$, $q = 1$ and therefore $k = 6$ in common for graphs $[\overline{4}1]$ and $[\overline{4}][2]$, which suggests that they map to certainly two binomial factors of $a_6$, respectively. A detailed discussion will be given below.

## 4. Evaluation of $a_k$

The nonadjacency number has been well utilized to rationalize the results of $a_k$'s for acyclic hydrocarbons [14]. This would be certainly extendable to alternants. In general, $(-1)^{k/2}a_k$ is equal to the number of selections of a set of edges and rings separated from one another having $k$ points in total [5]. With this in mind, we should consider the acyclic fragments jointly with cyclic ones when evaluating $a_k$'s of alternants. Let us describe these, one by one:

$a_2$ is simply equal to the number of edges involved in the graph, as indicated in eq. (8).

There are two nonadjacency species, namely two disjoint edges and a single 4-membered ring, which contribute to $a_4$, as follows:

$$a_4 = \binom{[2]}{2} - \binom{[3]}{1} - 2\binom{[\overline{4}]}{1} , \tag{10}$$

where

$$\binom{m}{n} = m!/[n!(m-n)!] .$$

The former two binomial numbers jointly represent the number of selecting two nonadjacent edges and the latter one corresponds to the selection of a single 4-membered ring which, in addition, contributes a weight equal to 2. The correspondence can be extended further to the relationship between each individual factor in eq. (10) and its specified graph. Indeed, there exactly exists a set of three graphs: $G_2([2]^2$, $[3]$, $[\overline{4}])$ satisfying the condition $p + 2q = 4$ and mapping one-to-one with the binomial factors in eq. (10). This suggests each binomial factor in $a_k$ equals the number of ways to select its mapping graph, regardless of whether its components are adjoint or not in the molecular graph. Parity of the binomial factor is dependent on the number of components that the mapping graph involves, as indicated in eq. (10).

Let us continue with higher members by means of the given argument. Accordingly, we can derive $a_6$ by first finding the whole of $G_3$, a graph set in which each member contains $p$ ring edges and $q$ chain edges satisfying eq. (9), namely $p + 2q = 6$. Then, binomial factors mapping to $G_3$ can readily be written. They are given as follows:

$$a_6 = -\binom{[2]}{3} + \binom{[3]}{1}\binom{[2]}{1}^{-2} - \binom{[4]}{1} - 2\binom{[31]}{1}$$
$$+2\binom{[\bar{4}]}{1}\binom{[2]}{1}^{-4} - 2\binom{[\bar{4}1]}{1} - 2\binom{[\bar{6}]}{1} \tag{11}$$

$G_3$: $[2]^3$, $[3][2]$, $[4]$, $[31]$, $[\bar{4}][2]$, $[\bar{4}1]$, $[\bar{6}]$,

where $a_6$ and $G_3$ are arranged in harmony with each other such that the one-to-one correspondence between binomial factors and mapping graphs is obvious.

Similar procedures can be used to derive $a_8$ with reference to $G_4$, a graph set in which each member satisfies $p + 2q = 8$. In the result given in eq. (12), $a_8$ is also arranged consistent with the sequence of $G_4$.

$$a_8 = \left\{\binom{[2]}{4} - \binom{[\bar{4}]}{1}\right\} - \left\{\binom{[3]}{1}\binom{[2]}{2}^{-2} - 4\binom{[\bar{4}]}{1}\right\} + \left\{\binom{[4]}{1}\binom{[2]}{1}^{-3} - 4\binom{[\bar{4}]}{1}\right\}$$
$$+ \left\{\binom{[3]}{2} - \binom{[4]}{1} - 3\binom{[31]}{1} - 2\binom{[\bar{4}]}{1}\right\} + 2\binom{[31]}{1}\binom{[2]}{1}^{-3} - \binom{[5]}{1} - 2\binom{[41]}{1}$$
$$-2\binom{[\bar{4}]}{1}\binom{[2]}{2}^{-4} + 2\binom{[\bar{4}1]}{1}\binom{[2]}{1}^{-5} + 2\left\{\binom{[\bar{6}]}{1}\binom{[2]}{1}^{-6} - \binom{[\bar{4}\,\bar{4}]}{1}\right\}$$
$$+2\left\{\binom{[\bar{4}]}{1}\binom{[3]}{1}^{-4} - 2\binom{[\bar{4}1]}{1}\right\} + 4\left\{\binom{[\bar{4}]}{2} - \binom{[\bar{4}|\bar{4}]}{1}\right\} - 2\binom{[\bar{4}2]}{1} - 2\binom{[\bar{4}11]}{1}$$
$$-2\binom{[\bar{4}101]}{1} - 2\binom{[\bar{6}1]}{1} - 2\binom{[\bar{8}]}{1} \tag{12}$$

$G_4$: $[2]^4$, $[3][2]^2$, $[4][2]$, $[3]^2$, $[31][2]$, $[5]$, $[41]$, $[\bar{4}][2]$, $[\bar{6}][2]$, $[\bar{4}][3]$,
$[\bar{4}]^2$, $[\bar{4}2]$, $[\bar{4}11]$, $[\bar{4}101]$, $[\bar{6}1]$, $[\bar{8}]$.

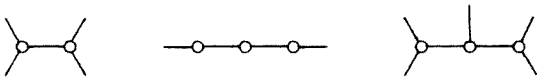
It seems a little complicated to look at these terms specified by graphs $[2]^4$, $[3][2]^2$, $[4][2]$, $[3]^2$, $[\bar{6}][2]$, $[\bar{4}][3]$ and $[\bar{4}]^2$, which are algebraic sums rather than single binomial numbers. As mentioned previously [14], one has to eliminate the trivial counts due to partial coincidence of edges or segments when a multi-component graph is selected. For example, as we consider the number of selections of $[3]^2$, we should take into account that selections where a pair of fragments [3], being partially overlapped by sharing an edge, are equal to 1 and 3 in graphs [4] and [31], respectively. On the other hand, there are two trivial selections of $[3]^2$ from graph $[\bar{4}]$. Therefore,

the binomial factor of $[3]^2$ given in eq. (12) is a combination of four terms. Other cases can be interpreted along similar lines. One interesting fact is that the fragment $[\overline{4}|\overline{4}]$ does not appear as a binomial factor in $a_8$, because its contribution has been included in the selection of species $[\overline{4}]^2$ and $[\overline{6}][2]$. It should be noted that in general there exists a weight equal to $2^{r+b}$, for the binomial factor specified by the graph involves $r$ rings and $b$ acyclic branch points.

$a_{10}$ and $a_{12}$ have also been computed. $a_{10}$ is rather lengthy, since the mapping set $G_5$ involves 41 members. $a_{12}$ becomes complicated because $G_6$ contains 105 members. Only $a_{10}$ is given in appendix 1.

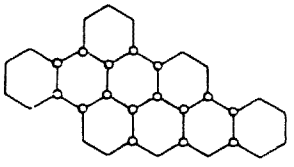
## 5. Benzenoid hydrocarbons

In principle, $a_k$'s with $k \leqslant 12$ for benzenoid hydrocarbons (BH) are reduced from the general formulas presented above by eliminating terms involving 4- and 8-membered rings. For better handling and implementation of these formulas, fragments conveniently enumerated should be adopted instead of those counted with difficulty. Thus, the following three branched species are feasibly introduced for simplifying formulas up to $a_8$:



(33) (222) (333)

Both (33) and (333) can be directly determined from the skeleton of branch points, and (222) depends solely on terminal hexagons. For instance, the branch point skeleton has been marked with circles in the following molecule



and it is straightforward to find (33) = 17, (222) = 5, (333) = 23 in it. In this way, $a_4$, $a_6$ and $a_8$ of BH are formulated in terms of topological variables and easily handled as follows:

$$a_4(\mathrm{BH}) = \tfrac{1}{2}(2[2]^2 - 9[2] + 6[1]) \tag{13}$$

$$a_6(\mathrm{BH}) = -\tfrac{1}{6}([2]^3 - 27[2]^2 + 116[2]) - [1](3[2] - 16) - (33) - 2[\overline{6}] \tag{14}$$

$$a_8(\mathrm{BH}) = \tfrac{1}{24}([2]^4 - 54[2]^3 + 707[2]^2 - 2772[2])$$

$$+ \tfrac{1}{2}[1](3[2]^2 - 59[2] + 9[1] + 201) - (33)([2] - 10)$$

$$- (222) - 7(333) + 2[\bar{6}]([2] - 6) - 2[\bar{6}1]\ . \qquad (15)$$

Recently, Dias gave $a_6(\mathrm{BH})$ as well as $a_8$(cata-BH) as follows, where cata-BH means cata-condensed BH [13]:

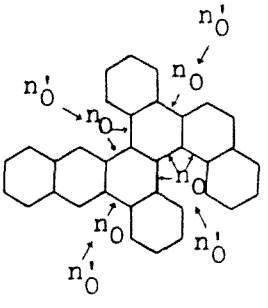
$$a_6(\mathrm{BH}) = -\tfrac{1}{6}(q^3 - 27q^2 + 146q + 36) - N_c(q - 22) - n_0 - 2r_6 \qquad (16)$$

$$a_8(\text{cata-BH}) = 4(q - 8) + 2(q - 10)(r_6 - 2) + 5(r_6 - 2)n_0 + n_0'$$

$$-2(n_4 - 2) + \tfrac{1}{24}(q - 7)(q - 6)(q - 5)(q - 4)$$

$$-\tfrac{50}{3}q_I^3 + 22q_I^2 - \tfrac{34}{3}q_I + 2, \qquad (17)$$

where $N_c$, $q$ and $r_6$ are identical to [1], [2] and $[\bar{6}]$, respectively. $n_0$ is defined as the number of bay regions, $n_0'$ is the number of separate bay regions, $n_4$ is the number of terminal hexagons and $q_I$ is the number of inner bonds. These are illustrated in fig. 3.




$n_0 = 7,\ n_0' = 4,\ n_4 = 4$

Fig. 3. Illustration of $n_0$, $n_0'$ and $n_4$.

One can easily find the equivalence between eqs. (14) and (16) by noticing the relation: $(33) = n_0 + 5[2] - 6([1] - 1)$. On the other hand, the following identities are valid for cata-BHs:

$$[1] = 4r_6 + 2, \quad [2] = 5r_6 + 1, \quad (33) = r_6 + n_0 - 1$$

$$(222) = 2n_4, \quad (333) = 3n_0 - n_0', \quad [\bar{6}1] = 4(r_6 - 1). \qquad (18)$$

Substituting eq. (18) into eq. (15) together with $q_I = r_6 - 1$, equation (17) is readily obtained.

## 6. Cata-condensed benzenoid hydrocarbons

The topology of cata-BH is well represented by its characteristic graph [19], which is defined by fixing a point in the center of each hexagon and then connecting adjacent points. Thus, a tree graph called a characteristic tree (CT) is formed (see fig. 4).

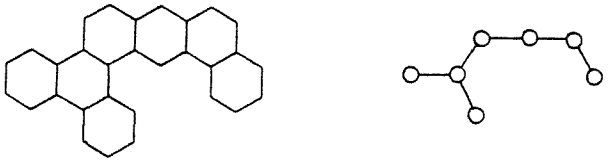



Fig. 4. Cata-BH and its CT graph.

In order to treat $a_k$'s up to $k = 12$, thirteen CT fragments, together with their symbols, are listed in fig. 5. One can easily deduce relations between molecular fragments (figs. 1–2) and CT fragments (fig. 5), which have been tabulated in appendix 2.

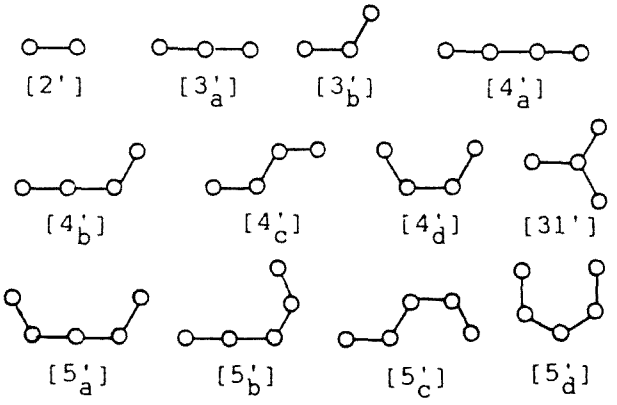



Fig. 5. Diagrams and symbols of CT fragments.

Based on these, the original $a_k$'s are reduced to succinct formulas in terms of CT fragments as variables:

$$a_2(\text{cata-BH}) = -(5[2'] + 6)$$

$$a_4(\text{cata-BH}) = 2^{-1}(25[2']^2 + 39[2'] + 18)$$

$$a_6(\text{cata-BH}) = -6^{-1}(125[2']^3 + 135[2']^2 + 106[2'] + 24) - [3'_b]$$

$$\begin{aligned} a_8(\text{cata-BH}) = {} & 24^{-1}(625[2']^4 - 150[2']^3 + 743[2']^2 - 168[2']) + [3'_b](5[2'] - 6) \\ & -2[3'_a] - [4'_d] \end{aligned}$$

$$\begin{aligned} a_{10}(\text{cata-BH}) = {} & -24^{-1}(625[2']^5 - 1500[2']^4 + 2915[2']^3 - 3180[2']^2 + 1356[2']) \\ & -2^{-1}[3'_b](25[2']^2 - 81[2'] + 100) + 2[3'_a](5[2'] - 12) \\ & +[4'_d](5[2'] - 10) - [4'_b] - [4'_c] - [5'_d] \end{aligned}$$

$$\begin{aligned} a_{12}(\text{cata-BH}) = {} & 144^{-1}(3125[2']^6 - 16875[2']^5 + 50975[2']^4 - 97233[2']^3 \\ & +102788[2']^2 - 42780[2']) + 6^{-1}[3'_b](125[2']^3 - 765[2']^2 \\ & +2092[2'] - 2103) + 2^{-1}[3'_b]^2 - [3'_a](25[2']^2 - 141[2'] \\ & +196) - 2^{-1}[4'_d](25[2']^2 - 121[2'] + 186) + [4'_b](5[2'] - 17) \\ & +[4'_c](5[2'] - 24) + [5'_d](5[2'] - 14) \\ & +2[4'_a] - 16[31'] - [5'_a] - [5'_b] - [5'_c] \ . \end{aligned} \tag{19}$$

In practice, these formulas are implemented conveniently because CT fragments can easily be counted. For some qualitative purpose, let us define the difference

$$\Delta a_k = a_k - a_k^0 \ , \tag{20}$$

where $a_k^0$ is a collection of terms involving the CT fragment $[2']$ only. Then we have

$$\Delta a_2 = \Delta a_4 = 0$$

$$\Delta a_6 = -[3'_b]$$

$$\Delta a_8 = [3'_b](5[2'] - 6) - 2[3'_a] - [4'_d]$$

$$\begin{aligned} \Delta a_{10} = {} & -2^{-1}[3'_b](25[2']^2 - 81[2'] + 100) + 2[3'_a](5[2'] - 12) \\ & +[4'_d](5[2'] - 10) - [4'_b] - [4'_c] - [5'_d] \end{aligned}$$

$$\Delta a_{12} = 6^{-1}([3'_b](125[2']^3 - 765[2']^2 + 2092[2'] - 2103) + 2[3'_b]^2$$
$$- [3'_a](25[2']^2 - 141[2'] + 196) - 2^{-1}[4'_a](25[2']^2 - 121[2'] + 186)$$
$$+ [4'_b](5[2'] - 17) + [4'_c](5[2'] - 24) + [5'_a](5[2'] - 14)$$
$$+ 2[4'_a] - 16[31'] - [5'_a] - [5'_b] - [5'_c] . \qquad (21)$$

These terms play the role of determining the relative stability among a set of isomers because for them $a_k^0$'s are constants.

In order to discuss the dependence of relative stability on $a_k$'s, let us review the Coulson formula [20] for total energy

$$E(G) = \frac{1}{\pi}\int_{-\infty}^{\infty} \frac{\ln|H_G(x)|}{x^2}\,dx , \qquad (22)$$

where $H_G(x)$ is a variant of the characteristic polynomial $P_G(x)$ in which all the coefficients are changed into positive ones, namely,

$$H_G(x) = 1 + |a_2|x^2 + |a_4|x^4 + \ldots + |a_N|x^N . \qquad (23)$$

Based on eq. (21), $H_G(x)$ is partitioned accordingly into two parts:

$$H_G(x) = H_G^0(x) + \Delta H_G(x) , \qquad (24)$$

where $H_G^0(x)$ depends on $|a_k^0|$'s being equal to one another among the isomers, but $H_G(x)$ is determined by $|\Delta a_k|$'s varying with respect to each individual isomer. Both $H_G^0(x)$ and $\Delta H_G(x)$ have the same sign. As a consequence of eqs. (22), (23) and (24), one can easily deduce that if isomers $G_1$ and $G_2$ satisfy

$$H_{G_1}(x) > H_{G_2}(x) ,$$

then they obey

$$E(G_1) > E(G_2)$$

i.e. $G_1$ is relatively more stable than $G_2$.

The validity of this result can be further attributed to the unequal role played by various fragments. Due to the positive and dominant contribution of species $[3'_b]$ in $\Delta H_G(x)$, it plays the decisive role of stabilization. In the case where isomers have

equal $[3'_b]$, species $[3'_a]$ and $[4'_d]$ become decisive, inducing the second effect of destabilization. Similar computations reveal that species $[4'_b]$, $[4'_c]$ and $[5'_d]$ play the role of stabilization in the third order, while $[4'_a]$, $[31']$, $[5'_a]$, $[5'_b]$ and $[5'_c]$ play the role of destabilization in the fourth order.

The above analysis stimulated us to determine the sequence of relative stability for a set of isomers by comparing the number of CT fragments one by one. We now illustrate the procedure by analyzing two series of isomers.

## 1. CATA-BHs WITH FOUR HEXAGONS

In total, there are five members of this isomer set, displayed in fig. 6. Their CT fragments have been counted and listed in table 1, together with Kekulé counts and total Hückel energy.

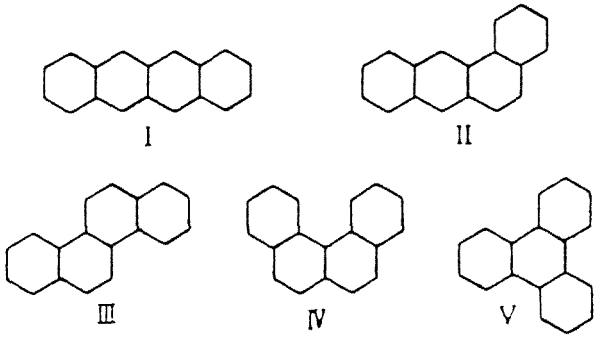



Fig. 6. Cata-BH isomers with four hexagons.

Table 1

| | I | II | III | IV | V |
|---|---|---|---|---|---|
| $[3'_b]$ | 0 | 1 | 2 | 2 | 3 |
| $[3'_a]$ | 2 | 1 | 0 | 0 | 0 |
| $[4'_d]$ | 0 | 0 | 0 | 1 | 0 |
| $K(G)$ | 5 | 7 | 8 | 8 | 9 |
| $E(G)$ | 24.931 | 25.101 | 25.192 | 25.187 | 25.274 |

Obviously, the counts listed in the first row of table 1 induces the following sequence:

$$V > IV,\ III > II > I\ ,$$

in which isomers III and IV can not be discriminated since they have equal $[3'_b]$. In addition, on examining the second and third rows one obtains

$$\text{III} > \text{IV}$$

because there are less $[4'_d]$ in III. Therefore, the whole sequence is determined completely in agreement with the sequence of $E(G)$ and better than that of $K(G)$.

## 2. CATA-BH ISOMERS CONSISTING OF FIVE HEXAGONS

There are twelve members in this isomer set, presented in fig. 7. The number of their CT fragments are tabulated in table 2, together with $E(G)$ and $K(G)$. From

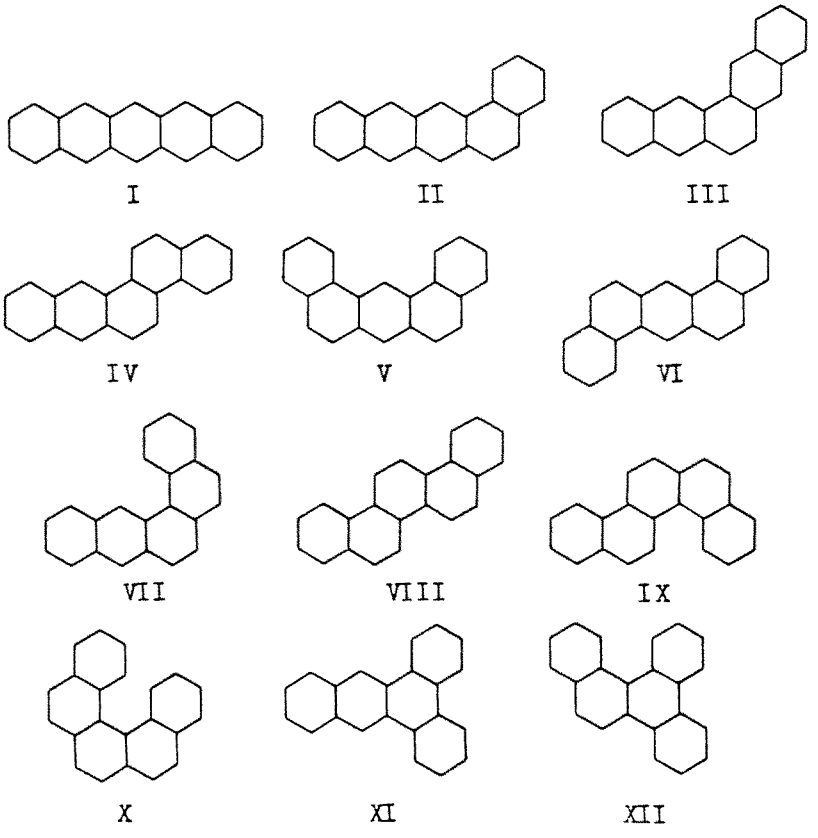



Fig. 7. Diagrams of cata-BHs with five hexagons.

$[3'_b]$, the sequence of relative stability is roughly divided into five groups, as indicated in the first row. On considering $[3'_a]$ and $[4'_d]$, the third and fourth groups are discriminated as follows:

Table 2

| | I | II | III | IV | V | VI | VII | VIII | IX | X | XI | XII |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $[3'_b]$ | 0 | 1 | 1 | 2 | 2 | 2 | 2 | 3 | 3 | 3 | 3 | 4 |
| $[3'_a]$ | 3 | 2 | 2 | 1 | 1 | 1 | 1 | 0 | 0 | 0 | 1 | 0 |
| $[4'_d]$ | 0 | 0 | 0 | 0 | 0 | 0 | 1 | 0 | 1 | 2 | 0 | 1 |
| $[4'_b]$ | 0 | 1 | 2 | 1 | 2 | 2 | 1 | 0 | 0 | 0 | 2 | 0 |
| $[4'_c]$ | 0 | 0 | 0 | 1 | 0 | 0 | 0 | 0 | 1 | 0 | 0 | 0 |
| $[5'_d]$ | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 1 | 0 | 1 |
| $[4'_a]$ | 2 | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| [31'] | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 1 | 1 |
| $[5'_a]$ | 0 | 0 | 0 | 0 | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| $[5'_b]$ | 0 | 0 | 0 | 0 | 0 | 0 | 1 | 0 | 0 | 0 | 0 | 0 |
| $[5'_c]$ | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 1 | 0 | 0 | 0 |
| $K(G)$ | 6 | 9 | 10 | 11 | 12 | 12 | 11 | 13 | 13 | 13 | 13 | 14 |
| $E(G)$ | 30.554 | 30.726 | 30.763 | 30.839 | 30.879 | 30.881 | 30.834 | 30.943 | 30.939 | 30.936 | 30.942 | 30.999 |

$$\text{VII} < \text{VI, V, IV} \qquad \text{X} < \text{XI} < \text{IX} < \text{VIII}.$$

Furthermore, by means of comparing $[4'_b]$, $[4'_c]$ and $[5'_d]$, we have

$$\text{II} < \text{III} \qquad \text{IV} < \text{V, VI},$$

and by continuously comparing $[5'_a]$, we obtain

$$\text{V} < \text{VI}.$$

Therefore, the final result is

$$\text{I} < \text{II} < \text{III} < \text{VII} < \text{IV} < \text{V} < \text{VI} < \text{X} < \text{XI} < \text{IX} < \text{VIII} < \text{XII},$$

which agrees well with $E(G)$ and much better than that of $K(G)$.

## References


[1] N. Biggs, *Algebraic Graph Theory* (Cambridge University Press, Cambridge, 1974).
[2] A. Graovac, I. Gutman and N. Trinajstić, *Topological Approach to the Chemistry of Conjugated Molecules* (Springer-Verlag, Berlin, 1977).
[3] A.C. Tang, Y.S. Kiang, G.S. Yan and S.S. Dia, *Graph Theoretical Molecular Orbitals* (Science Press, Beijing, 1986);
Y.S. Kiang, Int. J. Quant. Chem. S14(1980)541; 18(1980)331; S15(1981)293.
[4] H. Hosoya, Bull. Chem. Soc. Japan 44(1971)2332; Theor. Chem. Acta 25(1972)215;
H. Hosoya and M. Randić, ibid. 63(1983)473;
H. Hosoya and N. Ohkami, J. Comp. Chem. 4(1983)585.
[5] H. Sachs, Publ. Math. Debrecen 11(1963)119.
[6] E. Heilbronner, Helv. Chim. Acta 36(1952)170.
[7] I. Gutman, Chem. Soc. Faraday Trans. 2, 76(1980)1161;
I. Gutman, E.J. Rarrel and S.A. Wahid, J. Comb. Inf. Syst. Sci. 8(1983)159.
[8] M.V. Kaulgud and V.H. Chitgopkar, J. Chem. Soc. Faraday Trans. 2, 73(1977)1385; ibid. 74(1978)951.
[9] M. Randić, J. Comp. Chem. 3(1982)421.
[10] K. Balasubramanian, Int. J. Quant. Chem. 21(1982)581;
K. Balasubramanian and M. Randić, Theor. Chim. Acta 61(1982)307.
[11] B.J. McClelland, J. Chem. Soc. Faraday Trans. 2, 78(1982)991.
[12] S. El-Basil, Theor. Chim. Acta 65(1984)191; ibid. 64(1984)199.
[13] J.R. Dias, Theor. Chim. Acta 68(1985)107.
[14] Y. Jiang and A. Tang, Int. J. Quant. Chem. 29(1986)229.
[15] Y. Jiang and H. Zhang, Theor. Chim. Acta 75(1989)279.
[16] Y. Jiang, A. Tang and R. Hoffmann, Theor. Chim. Acta 66(1984)183.
[17] W. Cao and Y. Jiang, Acta Chim. Sin. 40(1982)880.
[18] G.G. Hall, Theor. Chim. Acta 70(1986)323.
[19] A.T. Balaban, *Chemical Applications of Graph Theory* (Academic Press, London-New York-San Francisco, 1976) p. 73.
[20] C.A. Coulson, Proc. Cambridge Phil. Soc. 36(1940)201.

## Appendix 1

THE FORMULA FOR $a_{10}$ AND ITS GRAPH SET $G_5$

$$
\begin{aligned}
a_{10} = &- \left\{\binom{[2]}{5} - \binom{[\bar{4}]}{1}\binom{[2]_1-4}{}\right\} + \left\{\binom{[3]}{1}\binom{[2]_3-2}{} - 4\binom{[\bar{4}]}{1}\binom{[2]_1-4}{} - 2\binom{[\bar{4}1]}{1}\right\} - \left\{\binom{[4]}{1}\binom{[2]_1-3}{} - 4\binom{[\bar{4}]}{1}\binom{[2]_1-4}{} - 2\binom{[\bar{4}1]}{1}\right\} \\
&- 2\left\{\binom{[31]}{1}\binom{[2]_2-3}{} - \binom{[\bar{4}1]}{1}\right\} - \left\{\left[\binom{[3]}{2} - \binom{[4]}{1} - 3\binom{[31]}{1} - 2\binom{[\bar{4}]}{1}\right]\binom{[2]_1-4}{} - 4\binom{[\bar{4}1]}{1}\right\} + \left\{\binom{[5]}{1}\binom{[2]_1-4}{} - 2\binom{[\bar{4}1]}{1}\right\} \\
&+ 2\left\{\binom{[41]}{1}\binom{[2]_1-4}{} - 2\binom{[\bar{4}1]}{1}\right\} + \left\{\binom{[4]}{1}\binom{[3]_1-2}{} - 2\binom{[5]}{1} - 4\binom{[41]}{1} - 8\binom{[\bar{4}]}{1} - 4\binom{[\bar{4}1]}{1}\right\} + 2\left\{\binom{[31]}{1}\binom{[3]_1-3}{} - \binom{[41]}{1} - \binom{[\bar{4}1]}{1}\right\} \\
&- \binom{[6]}{1} - 2\binom{[51]}{1} - 2\binom{[501]}{1} - 2\binom{[411]}{1} + 2\left\{\binom{[\bar{4}]}{1}\binom{[2]_3-4}{} - 2\binom{[\bar{4}|\bar{4}]}{1}\right\} - 2\left\{\binom{[\bar{4}1]}{1}\binom{[2]_2-5}{} - 4\binom{[\bar{4}|\bar{4}]}{1}\right\} \\
&- 2\left\{\binom{[\bar{6}]}{1}\binom{[2]_2-6}{} - \binom{[\bar{4}|\bar{4}]}{1}\binom{[2]_1-7}{}\right\} - 2\left\{\left[\binom{[\bar{4}]}{1}\binom{[3]_1-4}{} - 2\binom{[\bar{4}1]}{1}\right]\binom{[2]_1-6}{} - 4\binom{[\bar{4}|\bar{4}]}{1}\right\} + 2\left\{\binom{[\bar{4}2]}{1}\binom{[2]_1-6}{} - 4\binom{[\bar{4}|\bar{4}]}{1}\right\} \\
&+ 2\left\{\binom{[\bar{4}11]}{1}\binom{[2]_1-6}{} - 2\binom{[\bar{4}|\bar{4}]}{1}\right\} + 2\binom{[\bar{4}101]}{1}\binom{[2]_1-6}{} + 2\left\{\binom{[\bar{6}1]}{1}\binom{[2]_1-7}{} - \binom{[\bar{4}|\bar{4}1]}{1}\right\} - 4\left\{\binom{[\bar{4}]}{2} - \binom{[\bar{4}|\bar{4}]}{1}\right\}\binom{[2]_1-8}{} \\
&+ 2\left\{\binom{[\bar{8}]}{1}\binom{[2]_1-8}{} - \binom{[\bar{6}|\bar{4}]}{1}\right\} + 4\left\{\binom{[\bar{4}]}{1}\binom{[4]_1-4}{} - 2\binom{[\bar{4}1]}{1} - 2\binom{[\bar{4}2]}{1} - \binom{[\bar{4}11]}{1} - 2\binom{[\bar{4}|\bar{4}]}{1}\right\} + 4\left\{\binom{[\bar{4}]}{1}\binom{[31]}{1} - \binom{[\bar{4}1]}{1}\right\} \\
&+ 2\left\{\binom{[\bar{4}1]}{1}\binom{[3]_1-6}{} - \binom{[\bar{4}2]}{1} - 2\binom{[\bar{4}11]}{1} - 4\binom{[\bar{4}101]}{1} - 4\binom{[\bar{4}|\bar{4}]}{1}\right\} + 2\left\{\binom{[\bar{6}]}{1}\binom{[3]_1-6}{} - 2\binom{[\bar{6}1]}{1} - 4\binom{[\bar{4}|\bar{4}]}{1}\right\} \\
&+ 4\left\{\binom{[\bar{4}1]}{1}\binom{[\bar{4}]_1-1}{} - 4\binom{[\bar{4}|\bar{4}]}{1} - \binom{[\bar{4}|\bar{4}1]}{1}\right\} + 4\left\{\binom{[\bar{6}]}{1}\binom{[\bar{4}]}{1} - 2\binom{[\bar{4}|\bar{4}]}{1} - \binom{[\bar{6}|\bar{4}]}{1}\right\} - 2\binom{[\bar{4}3^1]}{1} - 4\binom{[\bar{4}3^2]}{1} - 2\binom{[\bar{4}21]}{1} \\
&- 2\binom{[\bar{4}201]}{1} - 2\binom{[\bar{4}111]}{1} - 4\binom{[\bar{4}-\bar{4}]}{1} - 2\binom{[\bar{6}2]}{1} - 2\binom{[\bar{6}11]}{1} - 2\binom{[\bar{6}101]}{1} - 2\binom{[\bar{6}1001]}{1} - 2\binom{[\bar{8}1]}{1} - 2\binom{[\bar{1}\bar{0}]}{1}
\end{aligned}
$$

$G_5$: $[2]^5$, $[3][2]^3$, $[4][2]^2$, $[31][2]^2$, $[3]^2[2]$, $[5][2]$, $[41][2]$, $[4][3]$, $[31][3]$, $[6]$, $[51]$, $[501]$, $[411]$, $[\bar{4}][2]^3$, $[\bar{4}1][2]^2$, $[\bar{6}][2]^2$, $[\bar{4}][3][2]$, $[\bar{4}2][2]$, $[\bar{4}11][2]$, $[\bar{4}101][2]$, $[\bar{6}1][2]$, $[\bar{4}]^2[2]$, $[\bar{8}][2]$, $[\bar{4}][4]$, $[\bar{4}][31]$, $[\bar{4}1][3]$, $[\bar{6}][3]$, $[\bar{4}1][\bar{4}]$, $[\bar{6}][\bar{4}]$, $[\bar{4}3^1]$, $[\bar{4}3^2]$, $[\bar{4}21]$, $[\bar{4}201]$, $[\bar{4}111]$, $[\bar{4}-\bar{4}]$, $[\bar{6}2]$, $[\bar{6}11]$, $[\bar{6}101]$, $[\bar{6}1001]$, $[\bar{8}1]$, $[\bar{1}\bar{0}]$.

## Appendix 2

RELATIONS BETWEEN CT FRAGMENTS AND MOLECULAR FRAGMENTS

$$
\begin{aligned}
[1] &= 4[2'] + 6 \\
[2] &= 5[2'] + 6 \\
[3] &= 8[2'] + 6 \\
[4] &= 12[2'] + 6 + [3'_b] \\
[31] &= 2[2'] \\
[5] &= 16[2'] + 6 + 2[3'_a] + 4[3'_b] + [4'_d] \\
[41] &= 8[2'] + 2[3'_b] \\
[6] &= 20[2'] + 6 + 8[3'_a] + 9[3'_b] + [4'_b] \\
&\quad + [4'_c] + 4[4'_d] + [5'_d] \\
[51] &= 8[2'] + 4[3'_a] + 6[3'_b] + 2[4'_d] \\
[501] &= 10[2'] + 6[3'_b] + [4'_d] \\
[411] &= [2'] + [3'_b] \\
[7] &= 18[2'] + 16[3'_a] + 16[3'_b] + 2[4'_a] \\
&\quad + 5[4'_b] + 6[4'_c] + 8[4'_d] + [5'_a] \\
&\quad + [5'_b] + [5'_c] + 4[5'_d] \\
[61] &= 8[2'] + 12[3'_a] + 10[3'_b] + 2[4'_b] \\
&\quad + 2[4'_c] + 6[4'_d] + 2[5'_d] \\
[601] &= 20[2'] + 12[3'_a] + 22[3'_b] + [4'_b] \\
&\quad + 2[4'_c] + 10[4'_d] + 2[5'_d] \\
[511] &= 4[2'] + 8[3'_b] + 2[4'_d] \\
[5101] &= 2[3'_a] + 2[3'_b] + [4'_d] \\
[502] &= 4[2'] + 4[3'_b] + 2[4'_d]
\end{aligned}
$$

$$
\begin{aligned}
[\bar{6}] &= [2'] + 1 \\
[\bar{6}1] &= 4[2'] \\
[\bar{6}2] &= 4[2'] + 2[3'_b] \\
[\bar{6}11] &= 2[2'] + [3'_b] \\
[\bar{6}101] &= 2[3'_a] + 2[3'_b] \\
[\bar{6}1001] &= 2[3'_a] + [3'_b] \\
[\bar{1}\bar{0}] &= [2'] \\
[\bar{6}3^1] &= 4[2'] + 4[3'_a] + 4[3'_b] \\
&\quad + 2[4'_d] \\
[\bar{6}3^2] &= 2[3'_b] \\
[\bar{6}2\bar{1}] &= 4[2'] + 4[3'_b] + 2[4'_d] \\
[\bar{6}201] &= 4[3'_a] + 4[3'_b] + [4'_b] \\
&\quad + 2[4'_c] + 2[4'_d] \\
[\bar{6}2001] &= 4[3'_a] + 2[3'_b] \\
&\quad + [4'_b] + 2[4'_c] \\
[\bar{6}111] &= 2[3'_b] \\
[\bar{6}1101] &= 4[3'_a] + 2[3'_b] + 6[31'] \\
[\bar{6}10101] &= 2[31'] \\
[\bar{6}\,|\,\bar{6}] &= [2'] \\
[\bar{1}\bar{0}1] &= 4[3'_a] + 4[3'_b]
\end{aligned}
$$

Other molecular fragments are all equal to zero, and

$$[31'] = [3'_a] + [3'_b] - [2'] + 1 \qquad ([2'] \neq 0).$$

Therefore, for cata-BH, eleven CT fragments are enough to express $u_k$ and $a_k$ for $k \leqslant 12$.