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# TOTAL RESONANT SEXTET BENZENOID HYDROCARBON ISOMERS AND THEIR MOLECULAR ORBITAL AND THERMODYNAMIC CHARACTERISTICS

JERRY RAY DIAS

*Department of Chemistry, University of Missouri, Kansas City, MO 64110 (U.S.A.)*

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## ABSTRACT

The more stable strain-free total resonant sextet isomers of benzenoid hydrocarbons are predicted to be probable combustion pollutants. These benzenoid hydrocarbons have been enumerated, and their topological characteristics examined. Total resonant sextet benzenoid isomers make up less than 1% of all the benzenoid hydrocarbons having formulas with $N_c$ divisible by 6. There is a thermodynamic preference for the larger and more highly condensed polycyclic aromatic hydrocarbon molecule. The Hückel molecular orbital (HMO) and thermodynamic parameters of these total resonant sextet benzenoid hydrocarbons have been computed and tabulated.

## INTRODUCTION

The structures of strictly peri-condensed benzenoid hydrocarbons (PAH6s) have been previously enumerated [1,2]. Strictly peri-condensed PAH6s have connected excised internal structures and corresponding formulas found on the left-hand diagonal of the formula periodic table for benzenoid polycyclic aromatic hydrocarbons. Since for a given number of carbon atoms strictly peri-condensed benzenoid hydrocarbons have the highest $p\pi$-energy and are free of strain energy, this class of macromolecular benzenoid compounds are predicted to have a higher relative probability of being formed during combustion/pyrolytic processes [2,3]. Another class of benzenoid hydrocarbons predicted to have a higher relative probability of forming via pyrolytic processes are total resonant sextet isomers found only in the $N_c \equiv 0(\mathrm{mod}6)$ column series of the formula periodic table for benzenoid polycyclic aromatic hydrocarbons [4,5]. Since a number of recent studies have begun to focus on the identification of macromolecular benzenoid hydrocarbons formed during various combustion related processes, this work was initiated to examine the stability and topological relationships of these potential pollutants [6–10].

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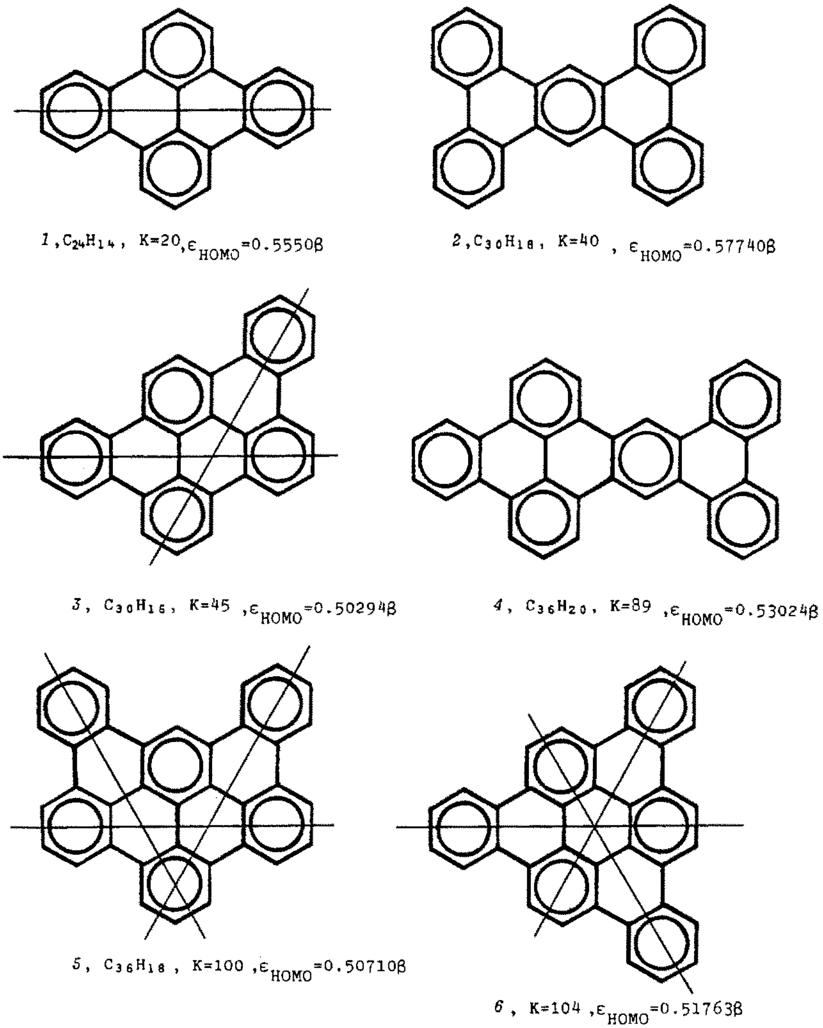
The rule of six had its genesis in the 1890s when Armstrong and Bamberger independently suggested that cyclic structures containing six benzene-like valencies should show unusual stability [11,12]. A valence-bond-like view of aromaticity in terms of resonant sextets was presented by Armitt and Robinson in the 1920s which was subsequently developed by Clar [13,14]. Quantitative resonant sextet relationships have recently been presented [15,16]. The Hosoya/Yamaguchi sextet polynomial, $B(G;X) = \Sigma_{k=0}^{m} r(G;k)X^k$, gives all the combinations of $k$ disjoint, but mutually resonant, sextets in the even vertex polyhex graph $G$ [17]. By definition, $r(G;0) = 1$. Also, $r(G;1) = r_6$, i.e., the number of hexagonal rings in $G$. The



*1*, $C_{24}H_{14}$, K=20, $\varepsilon_{HOMO}$=0.5550β

*2*, $C_{30}H_{18}$, K=40, $\varepsilon_{HOMO}$=0.57740β

*3*, $C_{30}H_{16}$, K=45, $\varepsilon_{HOMO}$=0.50294β

*4*, $C_{36}H_{20}$, K=89, $\varepsilon_{HOMO}$=0.53024β

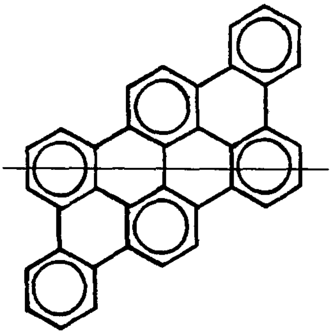
*5*, $C_{36}H_{18}$, K=100, $\varepsilon_{HOMO}$=0.50710β

*6*, K=104, $\varepsilon_{HOMO}$=0.51763β

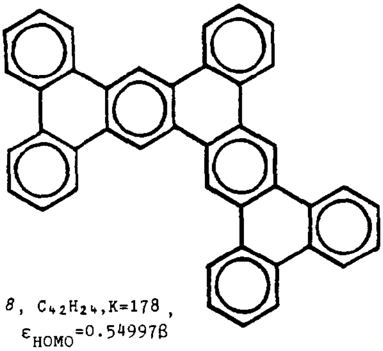
Fig. 1. Strain-free resonant sextet benzenoid isomers.

maximum number of mutually disjointed resonant sextets, $m$, present in any benzenoid graph is $m \leq N_c/6$ [4]; isomers for which $m = N_c/6$ is applicable are called total resonant sextet isomers and $r(G;m) = r(G;N_c/6) = 1$. A rapid algorithm for generating the sextet polynomial for cata-condensed and thin peri-condensed PAH6s has been described [18]. One can obtain the number of Kekulé structures ($K$) from the sextet polynomial via $B(G;X=1) = K$.

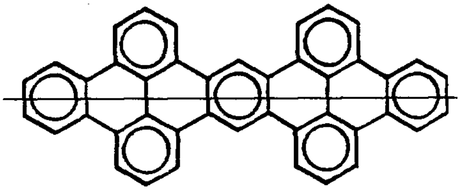
Previously we showed that total resonant sextet isomers were 2-factor (spanning) subgraphs composed exclusively of hexagonal components [4,5].



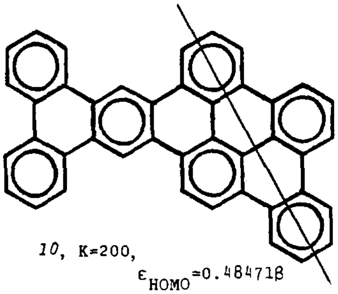
7, K=101, $\varepsilon_{HOMO}$=0.45191β



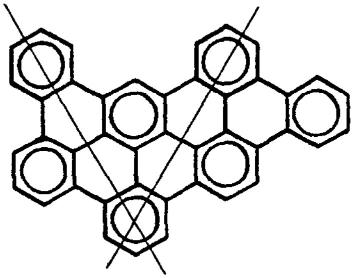
8, $C_{42}H_{24}$, K=178, $\varepsilon_{HOMO}$=0.54997β



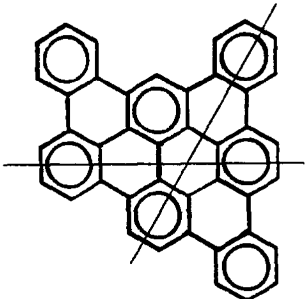
9, $C_{42}H_{22}$, K=198, $\varepsilon_{HOMO}$=0.49697β



10, K=200, $\varepsilon_{HOMO}$=0.48471β



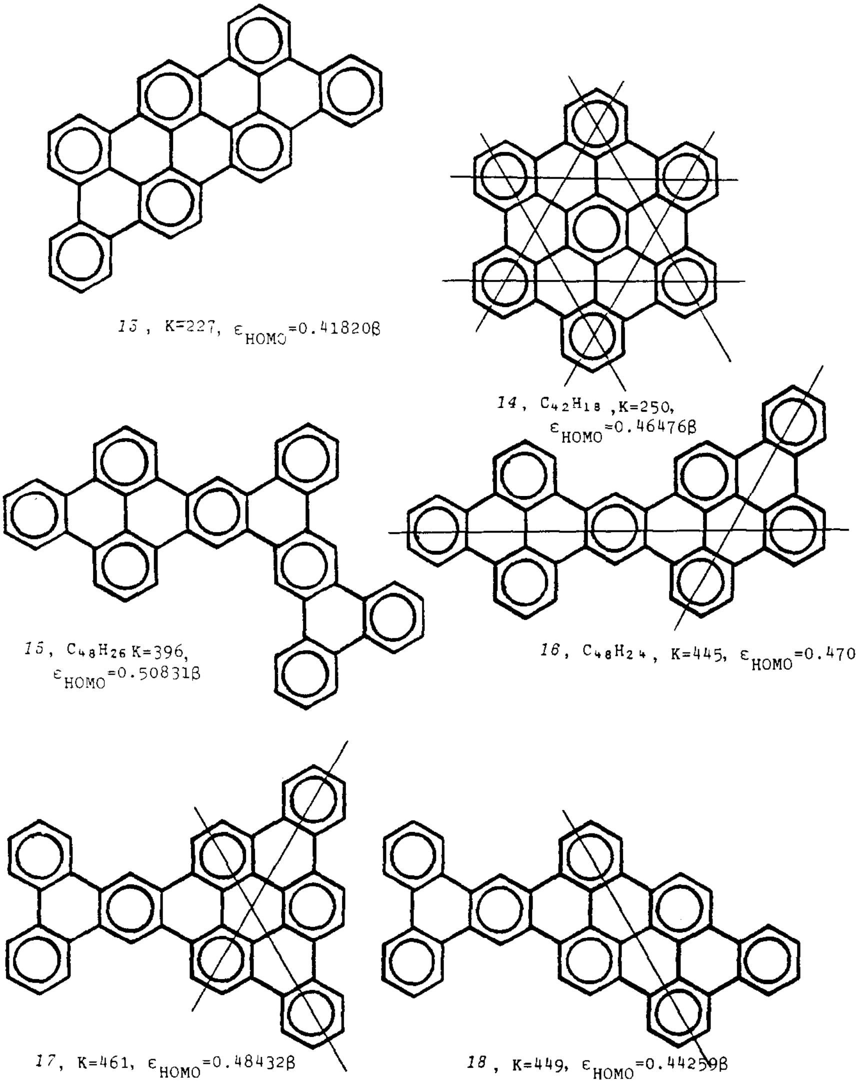
11, $C_{42}H_{20}$, K=225, $\varepsilon_{HOMO}$=0.45638β



12, K=230, $\varepsilon_{HOMO}$=0.45340β

Fig. 1. continued.

Total resonant sextet isomers are found only in $N_c \equiv 0(\mathrm{mod}6)$ columns of the formula periodic table for benzenoid polycyclic aromatic hydrocarbons where the number of hexagonal components is odd in the $N_c \equiv 2(\mathrm{mod}4)$ rows and even in the $N_c \equiv 0(\mathrm{mod}4)$ rows. Thus *5*, *6*, and *7* ($C_{36}H_{18}$ in Fig. 1) isomers have six (even number) hexagonal 2-factor components since $N_c = 36$ is divisible by both 6 and 4. Total resonant sextet benzenoid isomers have a greater number of distinct 2-factor subgraphs.



*13*, K=227, $\varepsilon_{HOMO}=0.41820\beta$

*14*, $C_{42}H_{18}$, K=250, $\varepsilon_{HOMO}=0.46476\beta$

*15*, $C_{48}H_{26}$ K=396, $\varepsilon_{HOMO}=0.50831\beta$

*16*, $C_{48}H_{24}$, K=445, $\varepsilon_{HOMO}=0.47032\beta$

*17*, K=461, $\varepsilon_{HOMO}=0.48432\beta$

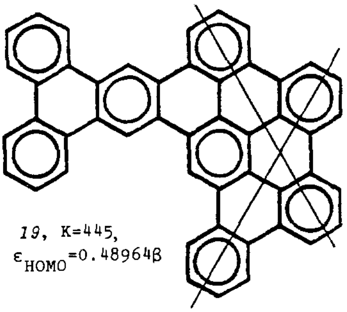
*18*, K=449, $\varepsilon_{HOMO}=0.44259\beta$

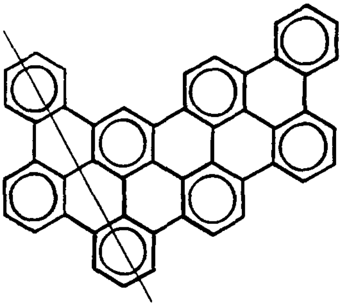
Fig. 1. continued.

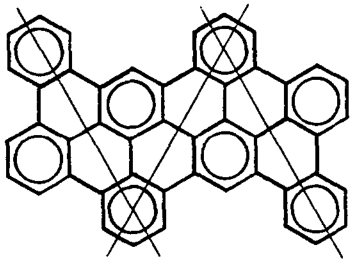
## RESULTS AND DISCUSSION

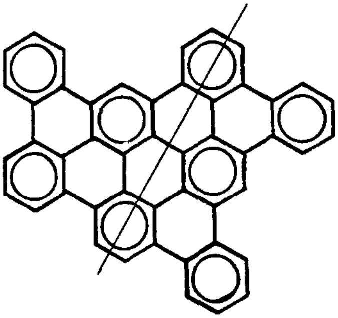
### *Enumeration of resonant sextet benzenoid hydrocarbons*

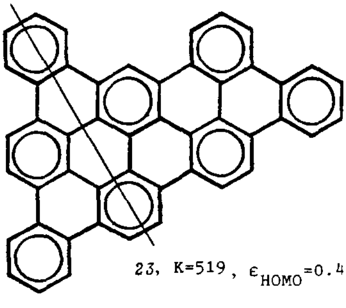
All the total resonant sextet isomers presented in Fig. 1 were enumerated by recursion. All resonant sextet isomers must have formulas such that the number of formula carbons ($N_c$) is divisible by six (i.e., $N_c \equiv 0(\mathrm{mod}6)$). Triphenylene ($C_{18}H_{12}$) is the smallest total resonant sextet benzenoid hydro-


19, K=445, $\varepsilon_{HOMO}=0.48964\beta$


20, $C_{48}H_{22}$, K=505, $\varepsilon_{HOMO}=0.42442\beta$


21, K=500, $\varepsilon_{HOMO}=0.45295\beta$


22, K=510, $\varepsilon_{HOMO}=0.43608\beta$


23, K=519, $\varepsilon_{HOMO}=0.42945\beta$

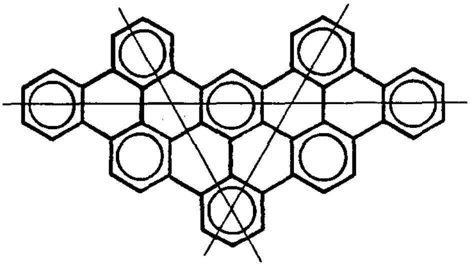
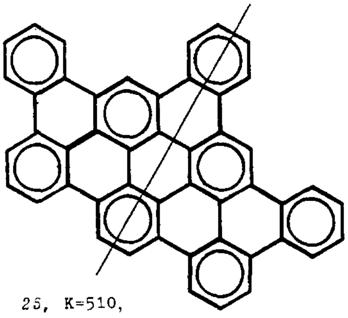

24, K=506, $\varepsilon_{HOMO}=0.42601\beta$

Fig. 1. continued.

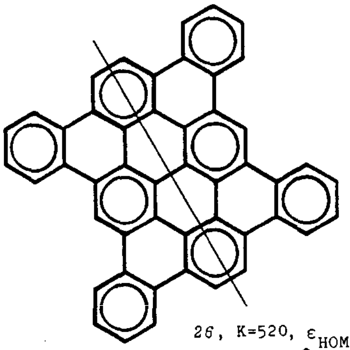
carbon followed by *1* (Fig. 1). Structures *2* and *3* both have five resonant sextets but *3* has two less hydrogens, four more internal third degree vertices ($N_{Ic} = 4$), and one more bonding edge than does *2*. Structure *4* is generated by the attachment of a $C_6H_2$ unit to *2* as shown in Fig. 2. The three different isomers of *5* to *7* can be generated by the three different attachments of $C_6H_2$ to *3*. All the other sextets in Fig. 1 were enumerated by this general recursive procedure. An alternant enumeration procedure would involve systematically excising them out from a "master structure" previously presented elsewhere [4]. However, this procedure would be less straightforward. No total resonant sextet isomers exist for $C_{54}H_{20}$.

Varying degrees of steric crowding occur in benzenoid hydrocarbons via transannular interactions [19]. Four principal levels of steric crowding are present in the concave bay regions of PAH6s. Phenanthrene has a 1,4-H,H (six-membered ring-like) interaction, benzo[*c*]phenanthrene has a 1,5-H,H interaction, dibenzo[*c,g*]phenanthrene has a 1,6-CH,CH interaction, and hexahelicene has two CH,CH and one CC,CC transannular interactions. Since the first interaction is sufficiently minimal, it often can be disregarded.

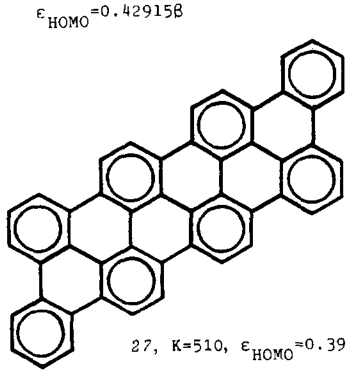
Only the minimally strained or essentially strain-free total resonant sextet isomers are enumerated in Fig. 1. Representative strained total resonant



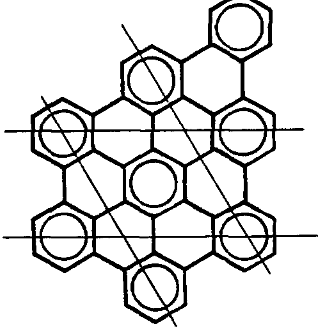
*25*, K=510, $\varepsilon_{HOMO}$=0.42915β



*26*, K=520, $\varepsilon_{HOMO}$=0.42507β



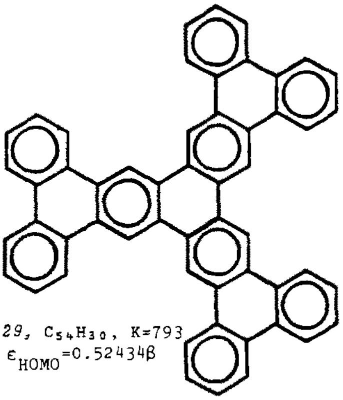
*27*, K=510, $\varepsilon_{HOMO}$=0.39141β



*28*, $C_{48}H_{20}$, K=575, $\varepsilon_{HOMO}$=0.41683β

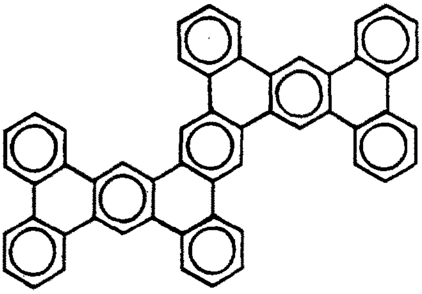
Fig. 1. continued.

sextet benzenoid isomers are presented in Fig. 3. These benzenoid hydrocarbons are strained because of transannular-hydrogen-pair interactions. During charring these strained hydrocarbons would be rapidly transformed to more stable strain-free and more peri-condensed total resonant sextet isomers (e.g., *61* to *3*). Strain-free total resonant sextet isomers have no proximate bay regions (i.e., $n_0 = n_0'$) but the strained ones do.

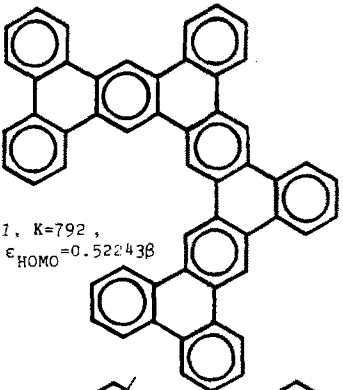


*29*, $C_{54}H_{30}$, K=793

$\varepsilon_{HOMO}=0.52434\beta$

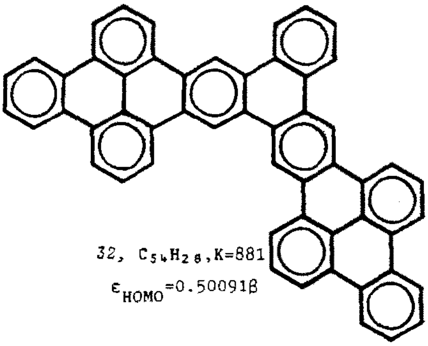


*30*, K=792, $\varepsilon_{HOMO}=0.52172\beta$



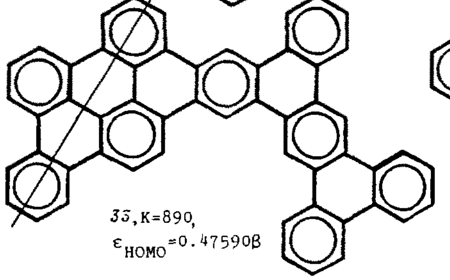
*31*, K=792 ,

$\varepsilon_{HOMO}=0.52243\beta$



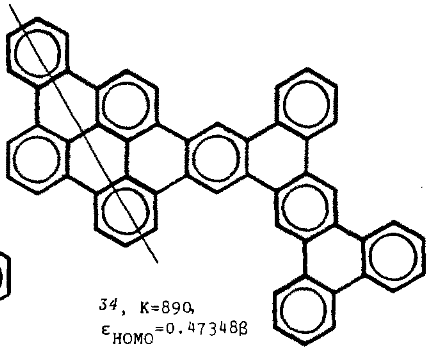
*32*, $C_{54}H_{28}$,K=881

$\varepsilon_{HOMO}=0.50091\beta$



*33*,K=890,

$\varepsilon_{HOMO}=0.47590\beta$

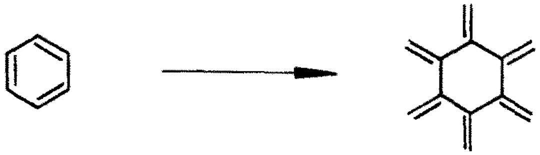


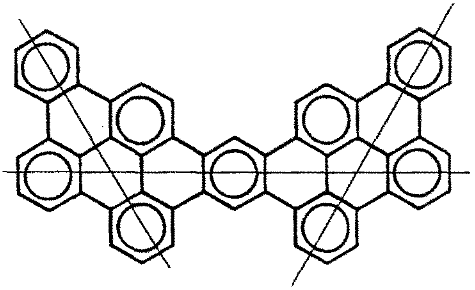
*34*, K=890,

$\varepsilon_{HOMO}=0.47348\beta$

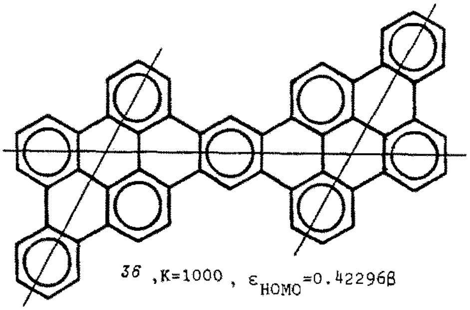
Fig. 1. continued.

Enumeration of macromolecular, strictly peri-condensed, total resonant sextet benzenoid hydrocarbons can be accomplished by the following prescription for constructing their excised internal structures. A corresponding excised internal structure is constructed from a small total resonant sextet benzenoid molecule by replacing all $=\underset{|}{C}-H$ units by $-\underset{|}{C}=CH_2$. By this process benzene becomes hexamethylenebenzene which is the excised internal structure of *14*. Two classes of macromolecular, strictly peri-condensed,

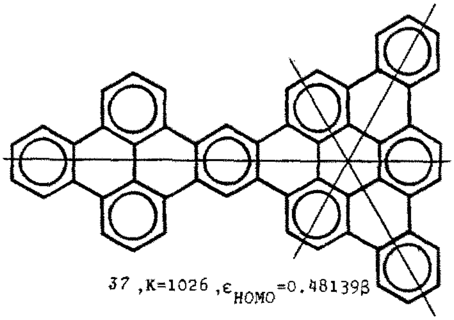




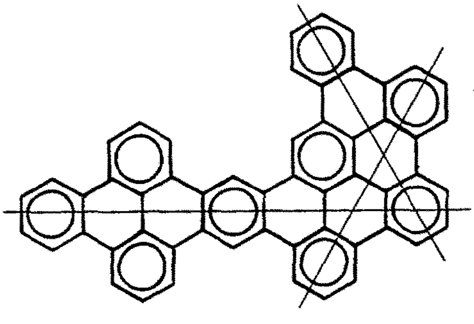
*35*, $C_{54}H_{26}$ ,K=1000 , $\varepsilon_{HOMO}=0.46309\beta$



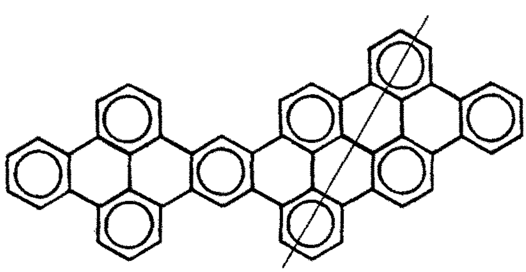
*36* ,K=1000 , $\varepsilon_{HOMO}=0.42296\beta$



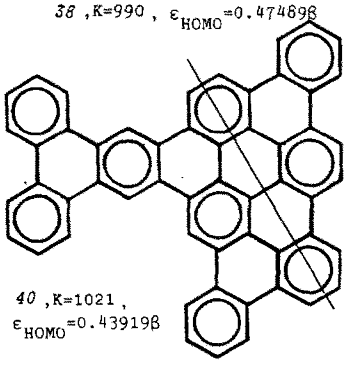
*37* ,K=1026 ,$\varepsilon_{HOMO}=0.48139\beta$



*38* ,K=990 , $\varepsilon_{HOMO}=0.47489\beta$



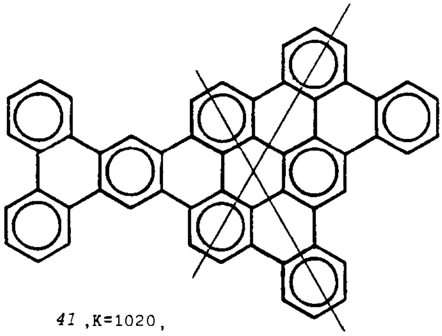
*39* , K=999 , $\varepsilon_{HOMO}=43497\beta$



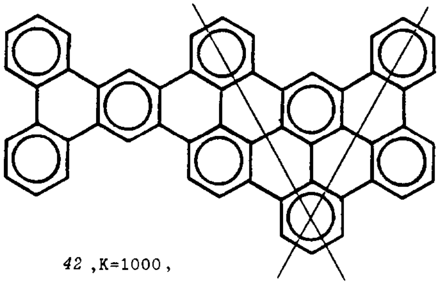
*40* ,K=1021 , $\varepsilon_{HOMO}=0.43919\beta$

Fig. 1. continued.

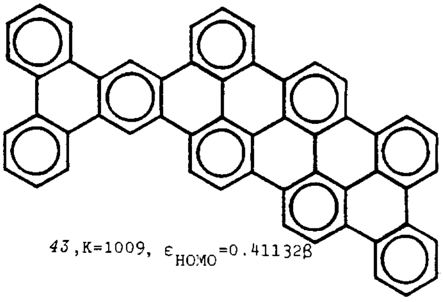
total resonant sextet benzenoid hydrocarbons can be generated in this way. The first class derive from benzene, biphenyl, terphenyl (the *m*- and *p*-isomers), etc., and the second class derive from the total resonant sextet structures shown in Fig. 1. The strictly peri-condensed total resonant sextet derived from biphenyl ($C_{12}H_{10}$) is the $C_{60}H_{22}$ structure shown in Fig. 4 and has a formula found in the $d_s = -4$ column series of the formula periodic table for PAH6 bezenoid hydrocarbons; similarly, the $C_{72}H_{24}$ strictly peri-condensed total resonant sextet found in the $d_s = -7$ column series derives



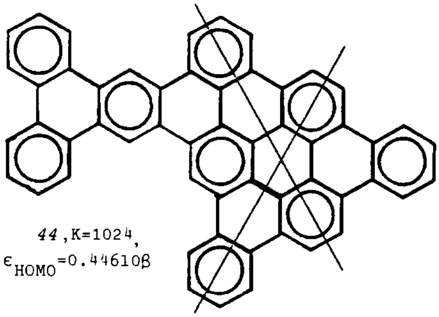
*41* ,K=1020, $\varepsilon_{HOMO}$=0.44707β



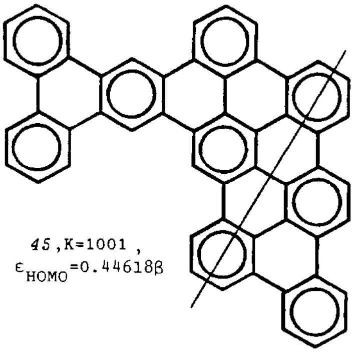
*42* ,K=1000, $\varepsilon_{HOMO}$=0.44774β



*43* ,K=1009, $\varepsilon_{HOMO}$=0.41132β



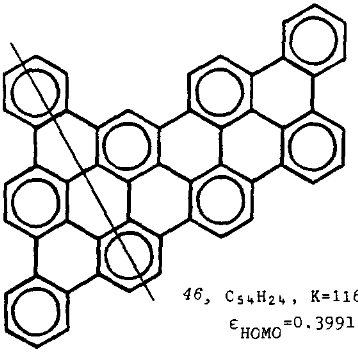
*44* ,K=1024, $\varepsilon_{HOMO}$=0.44610β



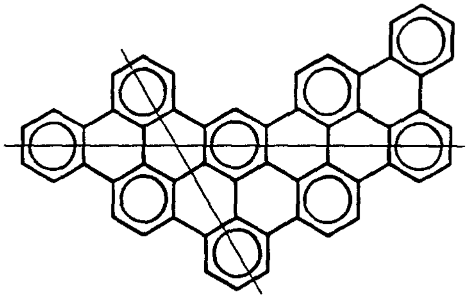
*45* ,K=1001 , $\varepsilon_{HOMO}$=0.44618β

Fig. 1. continued.

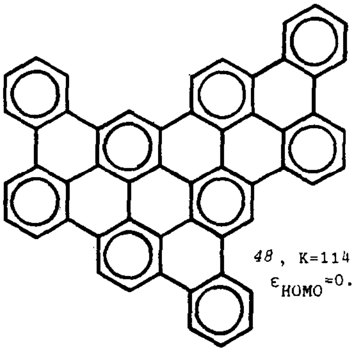
from triphenylene and is also shown in Fig. 4. Since there is only one benzenoid isomer of biphenyl or triphenylene, there is only one total resonant sextet isomer of $C_{60}H_{22}$ or $C_{72}H_{24}$, respectively, and these are the first formulas for which total resonant sextet isomers are possible in these respective column series. Attachment of a $C_6H_2$ unit to these first possible total resonant sextet structures leads to enumeration of other total resonant



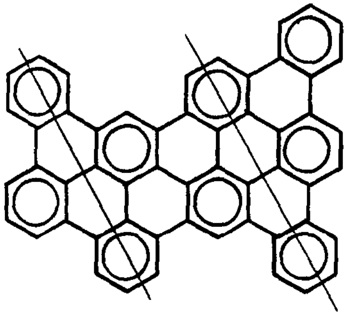
46, $C_{54}H_{24}$, K=1164, $\epsilon_{HOMO}=0.39914\beta$



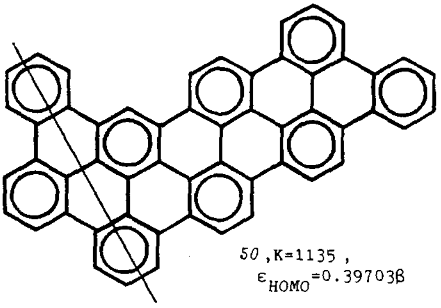
47, K=1136, $\epsilon_{HOMO}=0.40821\beta$



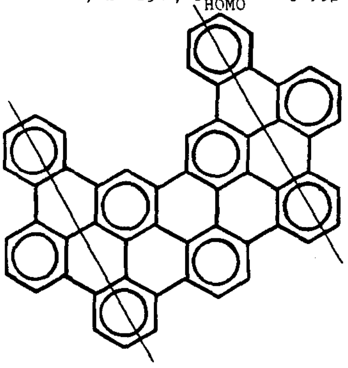
48, K=1149, $\epsilon_{HOMO}=0.43281\beta$



49, K=1150, $\epsilon_{HOMO}=0.43195\beta$



50, K=1135, $\epsilon_{HOMO}=0.39703\beta$

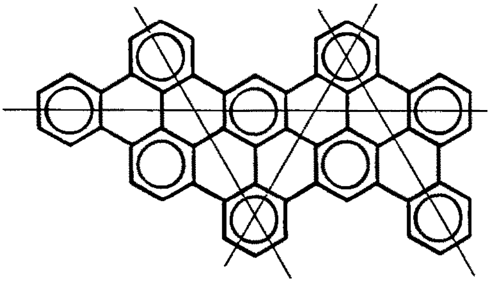


51, K=1125, $\epsilon_{HOMO}=0.43056\beta$

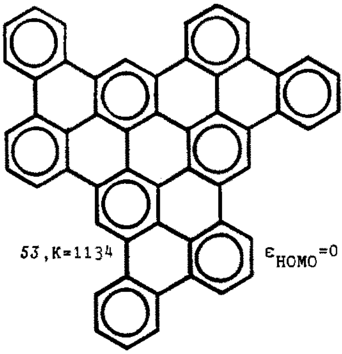
Fig. 1. continued.

sextet structures for these corresponding column series as illustrated in Fig. 5 for the $d_s = -1$ column series. Thus the number of strain-free resonant sextet isomers possible for $C_{42}H_{18}$, $C_{48}H_{20}$, and $C_{54}H_{22}$ are 1, 1 and 4, respectively for the $d_s = -1$ column series (Fig. 1). The number of strain-free total resonant sextet isomers with formulas $C_{60}H_{22}$, $C_{66}H_{24}$, $C_{72}H_{24}$, $C_{78}H_{26}$, $C_{84}H_{26}$, $C_{90}H_{28}$ and $C_{102}H_{30}$ are 1, 2, 1, 4, 1, 3 and 1, respectively.

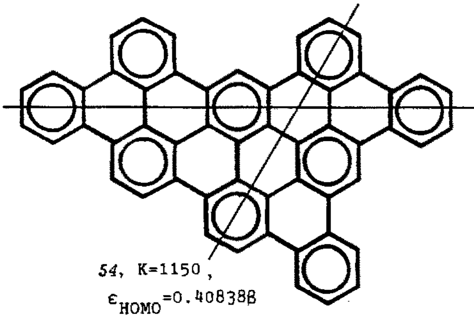
Synthesis of the total resonant sextet benzenoid hydrocarbons triphenylene, *1–6, 7, 9, 13, 14, 28, 61, 64* and *67* have been reported [19]. Although



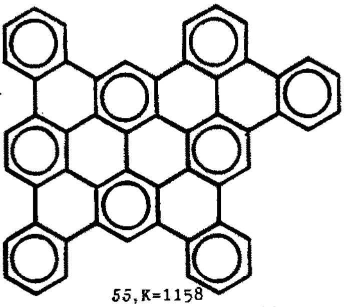
*52*, K=1125, $\varepsilon_{HOMO}=0.42299\beta$



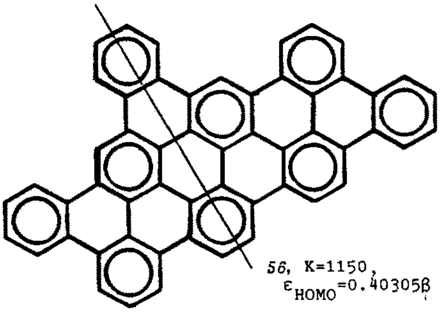
*53*, K=1134 $\varepsilon_{HOMO}=0.44277\beta$



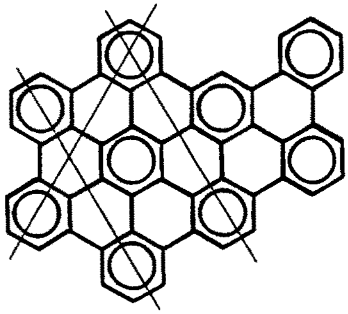
*54*, K=1150, $\varepsilon_{HOMO}=0.40838\beta$



*55*, K=1158 $\varepsilon_{HOMO}=0.43004\beta$

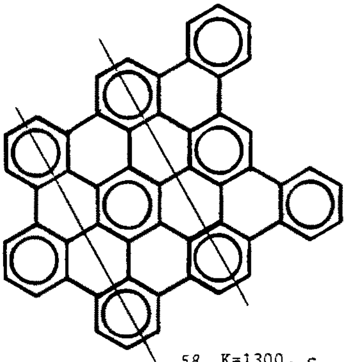


*56*, K=1150, $\varepsilon_{HOMO}=0.40305\beta$

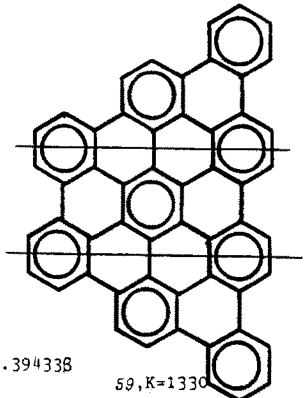


*57*, $C_{54}H_{22}$, K=1275, $\varepsilon_{HOMO}=0.40433\beta$

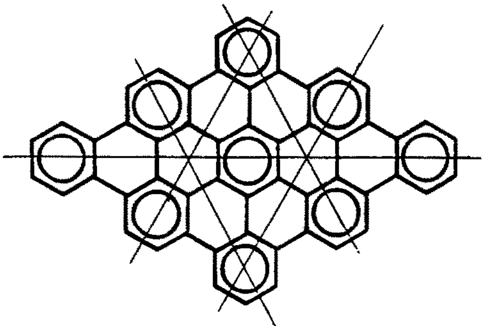
Fig. 1. continued.



58, K=1300, $\varepsilon_{HOMO}=0.39433\beta$



59, K=1330, $\varepsilon_{HOMO}=0.40123\beta$



60, K=1320, $\varepsilon_{HOMO}=0.38197\beta$

Fig. 1. continued.

*61*, *64* and *67* all possess considerable transannular strain only the latter has been reported to thermally decompose. Thermal decomposition of *67* to *14* and $H_2$ leads to relief of strain concomitant with an increase in resonance energy. Note that recent evidence suggests that the structure of *64* is incorrect [20]. Although only 12 of the 61 most stable total resonant sextet benzenoid hydrocarbons have been synthesized or identified in the environment, one is compelled to believe that it is only a matter of time until the

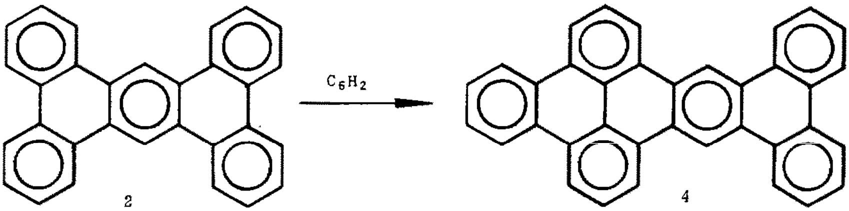
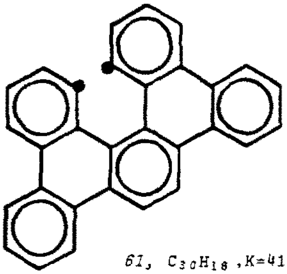
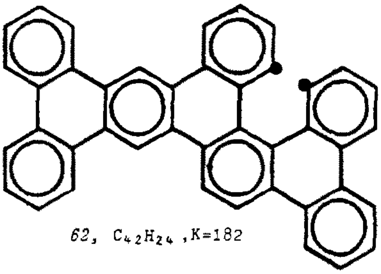


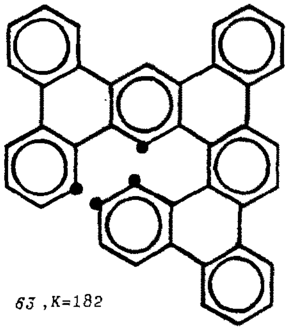
Fig. 2. Recursive construction of resonant sextets.



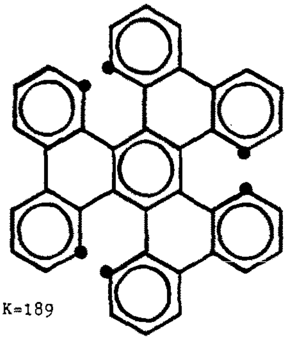
61, $C_{30}H_{18}$, K=41



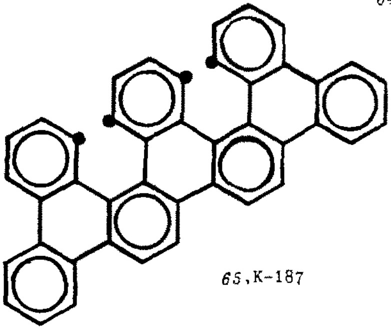
62, $C_{42}H_{24}$, K=182



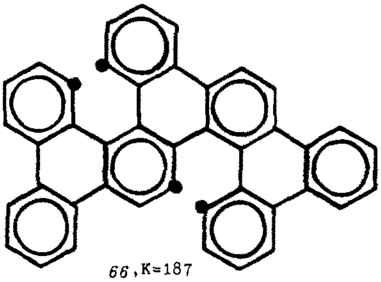
63, K=182



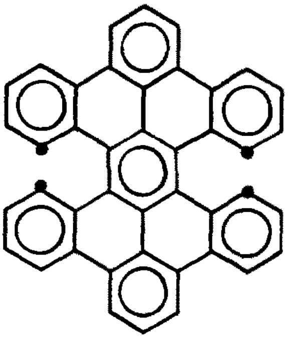
64, K=189



65, K-187

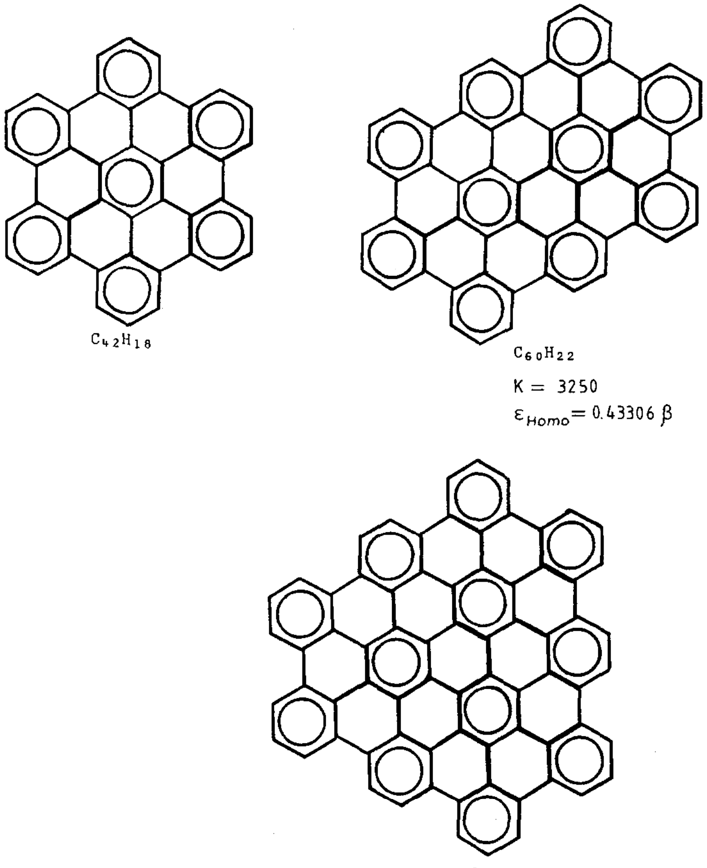


66, K=187



67, $C_{42}H_{22}$, K=200, $\epsilon_{HOMO}=0.40970\beta$

Fig. 3. Representative strained resonant sextet benzenoid isomers (regions of transannular strain are indicated by dots).



$C_{42}H_{18}$

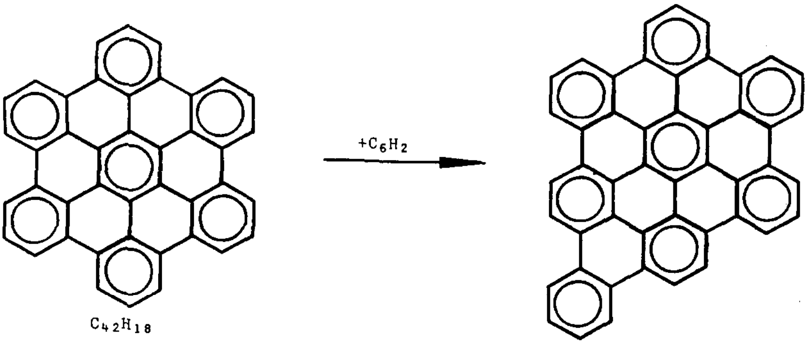
$C_{60}H_{22}$

$K = 3250$

$\varepsilon_{Homo} = 0.43306\ \beta$

$C_{72}H_{24}$

Fig. 4. Strictly peri-condensed total resonant sextets derived from permethylene analogs of benzene, biphenyl and triphenylene.



$C_{42}H_{18}$

$C_{48}H_{20}$

Fig. 5. Recursive enumeration of total resonant sextet isomers in the $d_s = -1$ column series.

TABLE 1

UV absorption bands for total resonant sextets [a]

| Compound | Formula | m.p. (°C) | $\lambda_\alpha$ | $\lambda_p$ | $\lambda_\beta$ | $\lambda_{\beta'}$ | Solvent |
|---|---|---|---|---|---|---|---|
| Triphenylene | $C_{18}H_{12}$ | 197 | 340.0 | 284.0 | 257.0 | | EtOH |
| *1* | $C_{24}H_{14}$ | 340–342 | 372.0 | 328.0 | 288.0 | 225.0 | PhH |
| *2* | $C_{30}H_{18}$ | 428–429 | 382.5 | 333.5 | 295.0 | | PhH |
| *3* | $C_{30}H_{16}$ | 388–389 | 401.0 | 374.0 | 300.0 | 234.0 | $C_6H_3Cl_3$ |
| *4* | $C_{36}H_{20}$ | 398–399 | 399.0 | 344.0 | 310.0 | 274.0 | $C_6H_3Cl_3$ |
| *5* | $C_{36}H_{18}$ | 434–436 | 430.0 | 365.0 | 334.0 | 238.0 | $C_6H_3Cl_3$ |
| *6* | $C_{36}H_{18}$ | 537–539 | 427.0 | 357.5 | 325.0 | | Dioxane |
| *7* | $C_{36}H_{18}$ | 530 | | 404.0 | 324.0 | | $C_6H_3Cl_3$ |
| *9* | $C_{42}H_{22}$ | 480–490 | 461.0 | 370.0 | 329.0 | | PhH |
| *13* | $C_{42}H_{20}$ | > 540 | | 435 | 331 | | $C_6H_3Cl_3$ |
| *14* | $C_{42}H_{18}$ | > 700 | 444.0 | 387.5 | 360.0 | | $C_6H_3Cl_3$ |
| *28* | $C_{48}H_{22}$ | | 462.0 | 429.0 | 380.0 | | |
| *61* | $C_{30}H_{18}$ | 275–276.5 | 348.0 | 325.0 | 284.0 | | PhH |
| *64* | $C_{42}H_{24}$ | 380 | 352.0 | 303.0 | 258.0 | | Dioxane |
| *67* | $C_{42}H_{22}$ | 481–482 [b] | | 467.0 | 353.0 | 309.0 | PhH |

[a] $\lambda$ in nm.

[b] At the m.p. *67* → *14* + $2H_2$.

remaining 50 total resonant sextet hydrocarbons are found [21]. Thus, this study of the properties of this class of compounds is undertaken to facilitate their identification in the environment. It is anticipated that this class of benzenoid hydrocarbons (*1* to *60*) because of their stability will not be carcinogenic. Large total resonant sextet benzenoid hydrocarbons have been recently suggested to be abundant in the interstellar medium surrounding carbon rich stars, and *14* has been studied in that regard [22]. An alternative synthesis of *3* using a photodehydrocyclization step in the presence of iodine has been published and an interesting nonplanar cata-condensed total resonant sextet, tribenzo[*f*,*l*,*r*]heptahelicene, was similarly synthesized [23,24]. Table 1 summarizes the melting points and principal $\lambda_{\max}$ values for the known total resonant sextet benzenoid hydrocarbon isomers.

### *Perimeter topology and polyhexes*

Previously the following four-variable equation was obtained

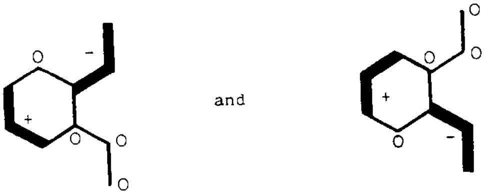
$$-n_0 + n_2 + 2n_3 + 3n_4 = 6$$

where $n_i$ is the number of peripheral regions on the boundary of a polyhex graph having $i$ adjacent second degree vertices. For example triphenylene ($C_{18}H_{12}$), the smallest total resonant sextet benzenoid hydrocarbon, has $n_0 = 3$ (i.e., the number of bay regions), $n_1 = n_2 = n_3 = 0$, and $n_4 = 3$ (i.e., the number of branches), and *3* in Fig. 1 has $n_0 = 5$, $n_1 = 0$, $n_2 = 1$, $n_3 = 2$, and $n_4 = 2$. Any set of strain-free resonant sextet benzenoid isomers has the same $e(3,3)_{\max}$ and $n_0(\max)$ values which are the maximum possible values for their given CH formula; $e(3,3)$ is the number of edges between two third degree vertices in the polyhex molecular graph. The maximum number of bay regions possessed by strain-free total resonant sextet PAH6s is given by $n_0(\max) = (\frac{1}{6})N_c + (\frac{1}{3})(d_s - 2)$. In general, the more bay regions a PAH6 has the more resonant sextets it can have and the more stable is the PAH6. Total resonant sextet PAH6 isomers also have the largest number of 2-factor subgraphs.

A Hamiltonian circuit is a one component 2-factor subgraph [4]. Previously we showed that a necessary, but not sufficient, prerequisite for a benzenoid polyhex graph to have a Hamiltonian circuit is that it must possess a formula found in the $N_c \equiv 2(\mathrm{mod}\ 4)$ rows of the formula periodic table for benzenoid polycyclic aromatic hydrocarbons. Thus, total resonant sextet structures *2, 3, 8, 10–14, 29–31, 33–36* and *40–60* all have Hamiltonian circuits. Structures *14* and *57–60* each have two distinct Hamiltonian circuits. The number of Kekulé structures for a total resonant sextet benzenoid is related to all the 2-factor subgraphs associated with it by $K \geqslant \Sigma_{2-F(G)} 2^h$ where $2 - F(G)$ is a 2-factor subgraph and $h$ is the number of hexagonal rings in the 2-factor.

## *Select eigenvalues of total resonant sextet isomers*

Structure *1* in Fig. 1 has a plane of symmetry passing through carbon vertices 6 and 13 along with the internal ones giving a 1,2-diethenylbenzene (1,2-divinylbenzene) fragment. Thus, structure *1* can be embedded by two 1,2-diethenylbenzene fragments where the carbon vertices on the mirror plane are node positions. As can be seen from Table 2, the eigenvalues of 1,2-diethylbenzene are among the eigenvalues of structure *1* (dibenzo-[*fg,op*]naphthacene), and the former is said to be subspectral to the latter. Furthermore, allyl can be embedded two different ways on 1,2-diethenylbenzene as shown by the following. Similarly, *1* can be embedded two different ways by allyl substructures and, therefore, allyl is subspectral to 1,2-diethenylbenzene and *1* and all have two $\varepsilon = \pm\sqrt{2}\beta$. In the same way phenanthrene is subspectral to *2*, 1-ethenylphenanthrene is subspectral to *5*, and benzo[*e*]pyrene is subspectral to *9*.



$\varepsilon = \pm\sqrt{2}$ and $\pm\sqrt{2}$

TABLE 2

Selected eigenvalues for some substructures of the resonant sextet benzenoids in Fig. 1

| Compound | $\pm\ \varepsilon,\beta$ |
|---|---|
| 1,2-Diethenylbenzene | 2.2469796, $\sqrt{2}$, $\sqrt{2}$, 0.8019377, 0.5549581 |
| Phenanthrene | 2.4347638, 1.9506269, 1.5162736, 1.3058003, 1.1423844, 0.7690515, 0.6052250 |
| 1-Ethenylphenanthrene | 2.4639357, 2.0420784, 1.5202323, 1.4985460, 1.1942476, 1.0, 0.7202815, 0.5070966 |
| Benzo[*e*]pyrene | 2.5935374, 2.1036348, 2.0150738, 1.5559393, 1.3508573, 1.3339274, 1.0, 1.0, 0.7180796, 0.4969706 |
| 1,8-Diethenylphenanthrene | 1.618034, 1.0, 0.618034 |
| Picene | 2.5347991, 2.2959921, 1.9363338, 1.5611195, 1.5344577, 1.3655852, 1.2016270, 1.0, 0.8594749, 0.6802949, 0.5019238 |
| Dibenzo[*fg*,*op*]naphthacene | 2.6343271, 2.2469784, 2.0288433, 1.8599418, $\sqrt{2}$, $\sqrt{2}$, 1.3306744, 1.1228080, 1.0, 0.8019375, 0.6732927, 0.5549579 |
| Tetrabenzo[*a*,*c*,*h*,*j*]anthracene | 2.4347638, 1.9506269, 1.5162736, 1.3058003, 1.1423844, 0.7690515, 0.6052250, 0.5774 |
| Tribenzo[*a*,*c*,*h*]anthracene | 0.6371, 0.5224 |
| 4-Ethenylpicene | 1.618034, 0.618034 |
| 3,6-Diethenylbenzo[*e*]pyrene | 1.618034, 0.618034 |

Structure *14* has three mirror planes which give a 1,8-diethenylphenanthrene fragment (Table 2) and both can be embedded by 1,3-butadiene. Structures *28* and *59* can be embedded by butadiene. Structure *58* has a mirror plane giving a 4-ethenylpicene fragment, and *60* has a mirror plane giving 3,6-diethenylbenzo[*e*]pyrene; these four latter structures can also be embedded by butadiene. Since 1,3-butadiene is subspectral to *14, 28, 58, 59* and *60* and their corresponding mirror fragments (Fig. 2), then all these structures have eigenvalues of $\varepsilon = \pm 0.618034$ and $\pm 1.618034$. Structure *6* can be embedded by benzene as shown below and therefore has $\varepsilon = \pm 1.0$, $\pm 1.0$ and $\pm 2.0\beta$. Picene is subspectral to *26*, and tribenzo[*a*,*c*,*h*]anthracene is subspectral to *31*. Many of the eigenvalues for these substructures, are presented in Table 2. The eigenvalues of the highest occupied MO for structures *1* to *60* were computed in this work (Fig. 1) and can be used to estimate their first ionization potentials [25].

Whenever a benzenoid structure can have a succession of edges bisected with a straight line drawn from one side of the molecule to the other with the terminal rings being symmetrically convex relative to the line, then those rings intersected by the line can be embedded with a perpendicular succession of ethene substructures and the benzenoid structure as a whole will have at least one eigenvalue pair of plus and minus one [26]. This straight line is called a selective lineation [26]. Thus all the resonant sextet benzenoids in Fig. 1 having selective lineations are indicated and have one pair of eigenvalues of $\varepsilon = \pm 1.0\beta$ for each line shown which were verified by solving the corresponding characteristic polynomials, $P(G;1) = 0$. Note that structures *14* and *60* have six and five, respectively, degenerate sets of $\varepsilon = \pm 1.0\beta$.

Structures *6*, *14*, and *29* each have a three-fold axis of symmetry and are consequently doubly degenerate in the given $\varepsilon_{\text{HOMO}}$ eigenvalues; likewise, triphenylene is doubly degenerate with $\varepsilon_{\text{HOMO}} = 0.6840\beta$. Substituting any hydrogen by a polyene group or any CH by a nitrogen on benzenoids *6*, *14*, and *29* will give corresponding daughter molecules still possessing the $\varepsilon_{\text{HOMO}}$ values given in Fig. 1. Resonant sextet *29* also has an eigenvalue of $\varepsilon = 0.63031\beta$.

*Energetic and stability factors*

Since resonance energy (RE) has been shown to be related to the logarithm of the Kekulé structure count ($K$), the $K$ values are given for all the total resonant sextet isomers shown in Fig. 1 [27]. Similarly, since the logarithm of the $a_{N-2}$ coefficient of the characteristic polynomial was also shown to be even more discriminating than log $K$, these values are also given in Table 3 [28]. The total $p\pi$-energies ($E_\pi$) in Table 3 were estimated by the method of Aihara in which he equates $E_\pi = 6.0846\beta \log Z$ where $Z = \Sigma_{j=0}^{N} | a_j |$ is the summation of the absolute values of the coefficients of the characteristic polynomial which were obtained by Balasubramanian's computer method [29,30]; the correct $E_\pi$ values for *1*, *2* and *6* are given in parentheses for comparison in Table 3. From Table 3 it is evident that for a given number of carbon atoms the strictly peri-condensed benzenoids have the highest $E_\pi$ values. This is illustrated by comparing *8* to *14* where $E_\pi$ steadily increases from $60.07\beta$ to $61.27\beta$. Parenthetically, *14* is the only strictly peri-condensed total resonant sextet in Fig. 1.

Through a vector addition analog method, we previously showed that total $p\pi$-energy ($E_\pi^{\text{L}}$) of a large benzenoid hydrocarbon can be estimated from the known $E_\pi$ values of smaller ones [3]. Thus when the number of carbon ($N_{\text{c}}^{\text{L}}$) and hydrogen ($N_{\text{H}}^{\text{L}}$) atoms of a large benzenoid hydrocarbon is related by $(N_{\text{c}}^{\text{L}}, N_{\text{H}}^{\text{L}}) = (N_{\text{c}}, N_{\text{H}}) + (N_{\text{c}}', N_{\text{H}}') = (N_{\text{c}} + N_{\text{c}}', N_{\text{H}} + N_{\text{H}}')$ to the number of carbon and hydrogen atoms of smaller benzenoid hydrocarbons, then $E_\pi^{\text{L}} = E_\pi + E_\pi'$. For example $(24,14) + (30,16) = (54,30)$ gives $E_\pi^{\text{L}} = 33.99\beta + 42.89\beta = 76.88\beta$ from *1* and *3* which compares favorably with $76.68\beta$ for *29* to *31* in Table 3; for triphenylene ($C_{18}H_{12}$), $E_\pi = 25.10\beta$ ($25.27\beta$), and $(18,12) + (36,18) = (54,30)$ gives $E_\pi^{\text{L}} = 25.10\beta + 51.79\beta = 76.89\beta$ for *29* to *31* where the $51.79\beta$ value comes from *7*. Similar examples should be evident to the reader for vector addition of benzene to *11–13* and *16–28*.

The thermal chemistry of large polycyclic aromatic hydrocarbons is fundamental to the chemistry of char formation and gasification. Most prior research on coal thermolysis has focussed on the early stages of reaction

TABLE 3

The values of $K$ and $|a_{N-2}|$ for all the resonant sextet structures in Fig. 1

| Compound | Formula | $\lvert a_{N-2}\rvert$ | $K$ | $E_\pi,\beta$ |
|---|---|---|---|---|
| *1* | $C_{24}H_{14}$ | 4496 | 20 | 33.99 (34.16) |
| *2* | $C_{30}H_{18}$ | 22449 | 40 | 42.29 (42.55) |
| *3* | $C_{30}H_{16}$ | 29326 | 45 | 42.89 |
| *4* | $C_{36}H_{20}$ | 136748 | 89 | 51.18 |
| *5* | $C_{36}H_{18}$ | 177775 | 100 | 51.78 |
| *6* | $C_{36}H_{18}$ | 189072 | 104 | 51.80 (51.98) |
| *7* | $C_{36}H_{18}$ | 182080 | 101 | 51.79 |
| *8* | $C_{42}H_{24}$ | 635865 | 178 | 59.49 |
| *9* | $C_{42}H_{22}$ | 803905 | 198 | 60.07 |
| *10* | $C_{42}H_{22}$ | 821888 | 200 | 60.08 |
| *11* | $C_{42}H_{20}$ | 1067661 | 225 | 60.68 |
| *12* | $C_{42}H_{20}$ | 1108284 | 230 | 60.69 |
| *13* | $C_{42}H_{20}$ | 1094577 | 227 | 60.69 |
| *14* | $C_{42}H_{18}$ | 1355625 | 250 | 61.27 |
| [a] | $C_{42}H_{16}$ | 917925 | 175 | 61.57 |
| *15* | $C_{48}H_{26}$ | 3655300 | 396 | 68.37 |
| *16* | $C_{48}H_{24}$ | 4710584 | 445 | 68.97 |
| *17* | $C_{48}H_{24}$ | 5018538 | 461 | 68.99 |
| *18* | $C_{48}H_{24}$ | 4820980 | 449 | 68.98 |
| *19* | $C_{48}H_{24}$ | 4718866 | 445 | 68.97 |
| *20* | $C_{48}H_{22}$ | 6245358 | 505 | 69.576 |
| *21* | $C_{48}H_{22}$ | 6102400 | 500 | 69.564 |
| *22* | $C_{48}H_{22}$ | 6337584 | 510 | 69.576 |
| *23* | $C_{48}H_{22}$ | 6528654 | 519 | 69.588 |
| *24* | $C_{48}H_{22}$ | 6255645 | 506 | 69.576 |
| *25* | $C_{48}H_{22}$ | 6346389 | 510 | 69.576 |
| *26* | $C_{48}H_{22}$ | 6568121 | 520 | 69.588 |
| *27* | $C_{48}H_{22}$ | 6418861 | 510 | 69.568 |
| *28* | $C_{48}H_{20}$ | 8246100 | 575 | 70.18 |
| [a] | $C_{48}H_{18}$ | – | 70–585 | – |
| *29* | $C_{54}H_{30}$ | 16421688 | 793 | 76.68 |
| *30* | $C_{54}H_{30}$ | 16380145 | 792 | 76.68 |
| *31* | $C_{54}H_{30}$ | 16379704 | 792 | 76.68 |
| *32* | $C_{54}H_{28}$ | 20606853 | 881 | 77.26 |
| *33* | $C_{54}H_{28}$ | 21063384 | 890 | 77.27 |
| *34* | $C_{54}H_{28}$ | 21065400 | 890 | 77.27 |
| *35* | $C_{54}H_{26}$ | 27071025 | 1000 | 77.87 |
| *36* | $C_{54}H_{26}$ | 27080241 | 1000 | 77.87 |
| *37* | $C_{54}H_{26}$ | 28261665 | 1026 | 77.88 |
| *38* | $C_{54}H_{26}$ | 26535384 | 990 | 77.86 |
| *39* | $C_{54}H_{26}$ | 27102591 | 999 | 77.87 |
| *40* | $C_{54}H_{26}$ | 28222064 | 1021 | 77.88 |
| *41* | $C_{54}H_{26}$ | 28170279 | 1020 | 77.88 |
| *42* | $C_{54}H_{26}$ | 27157871 | 1000 | 77.87 |
| *43* | $C_{54}H_{26}$ | 27810402 | 1009 | 77.88 |
| *44* | $C_{54}H_{26}$ | 28305680 | 1024 | 77.88 |
| *45* | $C_{54}H_{26}$ | 27208766 | 1001 | 77.87 |
| *46* | $C_{54}H_{24}$ | 37516171 | 1164 | 78.49 |

TABLE 3 (continued)

| Compound | Formula | $\lvert a_{N-2} \rvert$ | $K$ | $E_\pi, \beta$ |
|---|---|---|---|---|
| *47* | $C_{54}H_{24}$ | 35911552 | 1136 | 78.47 |
| *48* | $C_{54}H_{24}$ | 36525951 | 1149 | 78.48 |
| *49* | $C_{54}H_{24}$ | 36506224 | 1150 | 78.48 |
| *50* | $C_{54}H_{24}$ | 35949121 | 1135 | 78.47 |
| *51* | $C_{54}H_{24}$ | 35103151 | 1125 | 78.46 |
| *52* | $C_{55}H_{24}$ | 35110351 | 1125 | 78.46 |
| *53* | $C_{54}H_{24}$ | 35646156 | 1134 | 78.47 |
| *54* | $C_{54}H_{24}$ | 36625841 | 1150 | 78.48 |
| *55* | $C_{54}H_{24}$ | 37048113 | 1158 | 78.49 |
| *56* | $C_{54}H_{24}$ | 36681629 | 1150 | 78.48 |
| *57* | $C_{54}H_{22}$ | 46157775 | 1275 | 79.07 |
| *58* | $C_{54}H_{22}$ | 47931975 | 1300 | 79.08 |
| *59* | $C_{54}H_{22}$ | 49688216 | 1330 | 79.09 |
| *60* | $C_{54}H_{22}$ | 49306081 | 1320 | 79.09 |
| [b] | $C_{54}H_{20}$ | – | – | – |
| [a] | $C_{54}H_{18}$ | 33696516 | 980 | 79.89 |
| *61* | $C_{30}H_{18}$ | 23421 | 41 | – |
| *62* | $C_{42}H_{24}$ | 662568 | 182 | – |
| *63* | $C_{42}H_{24}$ | 662757 | 182 | – |
| *64* | $C_{42}H_{24}$ | 714861 | 189 | – |
| *65* | $C_{42}H_{24}$ | 694941 | 187 | – |
| *66* | $C_{42}H_{24}$ | 695292 | 187 | – |

[a] Strictly peri-condensed benzenoids, no resonant sextet isomers of this formula exist.

[b] No resonant sextet isomers of this formula exist.

where the primary attention has been with the breaking of weaker aliphatic bonds external to the indigenous aromatic moieties rather than the reactions of these aromatic units and the formation of additional aromatic units in the later reaction stages. A consistent general result in pyrolytic studies is that only a relatively small number of elementary, single-step reactions are necessary for describing a wide range of complex reaction systems. Char formation precedes gasification as one moves through the combustion front from the air zone to the solid fuel zone. The combustion/air interface becomes depleted of oxygen as one moves toward the solid fuel phase. It is speculated that the later reaction stage of char formation involves a preponderance of formation of the more stable strictly peri-condensed and resonant sextet polycyclic aromatic hydrocarbons with the strained resonant sextets being transformed to nonstrained and more peri-condensed ones. For example, PAH6 *61* can react with one oxygen radical in a rarefied air/solid fuel layer to form water and PAH6 *3* with a net gain in $p\pi$-energy; $E_\pi = 42.3\beta$ for *61* goes to $E_\pi = 42.9\beta$ for *3*. Similarly, during charring *62, 63, 64, 65* and *66* would convert to *10, 12, 14, 13* and *11*, respectively. Thus, the relief of strain energy and the gain in $E_\pi$ both contribute to the driving force in the final stage of char formation.

Thermodynamic quantities for the minimally strained total resonant sextets *1* to *60* have been computed using Benson's group additivity method and are summarized in Table 4 [31,32]. From the data in this table, it is

TABLE 4

Calculation gas phase standard thermochemical quantities for total resonant sextet isomers

| Compound | Point group symmetry [a] | $\Delta H_f^0(298)$ (kcal mol$^{-1}$) | $S^0(298)$ (cal mol$^{-1}$ K$^{-1}$) |
|---|---|---|---|
| *1* | $D_{2h}(4)$ | 78.7 | 122.3 |
| *2* | $D_{2h}(4)$ | 103.8 | 144.7 |
| *3* | $C_{2v}(2)$ | 95.6 | 140.4 |
| *4* | $C_{2v}(2)$ | 120.7 | 162.8 |
| *5* | $C_{2v}(2)$ | 112.5 | 157.1 |
| *6* | $D_{3h}(6)$ | 112.5 | 154.9 |
| *7* | $C_{2h}(2)$ | 112.5 | 157.1 |
| *8* | $C_{2h}(2)$ | 145.8 | 185.3 |
| *9* | $D_{2h}(4)$ | 137.6 | 178.1 |
| *10* | $C_s(1)$ | 137.6 | 180.9 |
| *11,12* | $C_s(1)$ | 129.4 | 175.2 |
| *13* | $C_{2v}(2)$ | 129.4 | 173.8 |
| *14* | $D_{3h}(6)$ | 121.2 | 165.8 |
| *15* | $C_s(1)$ | 162.7 | 203.4 |
| *16* | $C_s(1)$ | 154.5 | 197.6 |
| *17* | $C_{2v}(2)$ | 154.5 | 196.2 |
| *18,19* | $C_s(1)$ | 154.5 | 197.6 |
| *20* | $C_s(1)$ | 146.3 | 191.9 |
| *21* | $C_{2h}(2)$ | 146.3 | 190.5 |
| *22,23* | $C_s(1)$ | 146.3 | 191.9 |
| *24,25* | $C_{2v}(2)$ | 146.3 | 190.5 |
| *26* | $D_{2h}(4)$ | 146.3 | 189.1 |
| *27* | $C_{2h}(2)$ | 146.3 | 190.5 |
| *28* | $C_{2v}(2)$ | 138.1 | 184.7 |
| *29* | $D_{3h}(6)$ | 187.8 | 225.9 |
| *30* | $C_{2h}(2)$ | 187.8 | 224.5 |
| *31* | $C_{2v}(2)$ | 187.8 | 224.5 |
| *32* | $C_{2v}(2)$ | 179.6 | 218.7 |
| *33,34* | $C_s(1)$ | 179.6 | 220.1 |
| *35* | $C_{2v}(2)$ | 171.4 | 212.9 |
| *36* | $C_{2h}(2)$ | 171.4 | 212.9 |
| *37* | $C_{2v}(2)$ | 171.4 | 212.9 |
| *38–45* | $C_s(1)$ | 171.4 | 214.3 |
| *46–50* | $C_s(1)$ | 163.2 | 208.6 |
| *51* | $C_{2v}(2)$ | 163.2 | 207.2 |
| *52* | $C_s(1)$ | 163.2 | 208.6 |
| *53* | $C_{3h}(3)$ | 163.2 | 206.4 |
| *54–56* | $C_s(1)$ | 163.2 | 208.6 |
| *57* | $C_s(1)$ | 155.0 | 202.8 |
| *58,59* | $C_{2v}(2)$ | 155.0 | 201.4 |
| *60* | $D_{2h}(4)$ | 155.0 | 200.0 |

[a] Symmetry number ($\sigma$) in parentheses.

TABLE 5

Gas phase standard free energy of formation per carbon atom for total resonant sextet benzenoid hydrocarbons

| Compound | Formula | $\Delta G^0(298)/N_c$ (kcal mol$^{-1}$) |
|---|---|---|
| *1* | $C_{24}H_{14}$ | 1.760 |
| *2* | $C_{30}H_{18}$ | 2.022 |
| *3* | $C_{30}H_{16}$ | 1.792 |
| *4* | $C_{36}H_{20}$ | 2.005 |
| *5* | $C_{36}H_{18}$ | 1.824 |
| *6* | $C_{36}H_{18}$ | 1.842 |
| *7* | $C_{36}H_{18}$ | 1.824 |
| *8* | $C_{42}H_{24}$ | 2.156 |
| *9* | $C_{42}H_{22}$ | 2.012 |
| *10* | $C_{42}H_{22}$ | 1.992 |
| *11,12* | $C_{42}H_{20}$ | 1.837 |
| *13* | $C_{42}H_{20}$ | 1.847 |
| *14* | $C_{42}H_{18}$ | 1.709 |
| *15* | $C_{48}H_{26}$ | 2.126 |
| *16* | $C_{48}H_{24}$ | 1.992 |
| *17* | $C_{48}H_{24}$ | 2.000 |
| *18,19* | $C_{48}H_{24}$ | 1.992 |
| *20* | $C_{48}H_{22}$ | 1.856 |
| *21* | $C_{48}H_{22}$ | 2.865 |
| *22,23* | $C_{48}H_{22}$ | 1.856 |
| *24,25* | $C_{48}H_{22}$ | 1.865 |
| *26* | $C_{48}H_{22}$ | 1.874 |
| *27* | $C_{48}H_{22}$ | 1.865 |
| *28* | $C_{48}H_{20}$ | 1.730 |
| *29* | $C_{54}H_{30}$ | 2.231 |
| *30* | $C_{54}H_{30}$ | 2.238 |
| *31* | $C_{54}H_{30}$ | 2.238 |
| *32* | $C_{54}H_{28}$ | 2.119 |
| *33,34* | $C_{54}H_{28}$ | 2.111 |
| *35* | $C_{54}H_{26}$ | 1.999 |
| *36* | $C_{54}H_{26}$ | 1.999 |
| *37* | $C_{54}H_{26}$ | 1.999 |
| *38–45* | $C_{54}H_{26}$ | 1.991 |
| *46–50* | $C_{54}H_{24}$ | 1.871 |
| *51* | $C_{54}H_{24}$ | 1.878 |
| *52* | $C_{54}H_{24}$ | 1.871 |
| *53* | $C_{54}H_{24}$ | 1.883 |
| *54–56* | $C_{54}H_{24}$ | 1.871 |
| *57* | $C_{54}H_{22}$ | 1.751 |
| *58,59* | $C_{54}H_{22}$ | 1.756 |
| *60* | $C_{54}H_{22}$ | 1.766 |
| Graphite | | 0.9075 |
| Infinite acene | | 3.0767 |

evident that for a given number of carbon atoms ($N_c$) in a benzenoid group as the number of internal carbon atoms increase $\Delta G^0(298)$ decreases, i.e., becomes more negative. This is the result of trading two $C_B$–(H) group terms by two $C_{FR}$–$(C_{FR})_3$ group terms with each increase of $\Delta N_{Ic} = 2$ while holding $N_c$ fixed. Thus for a given $N_c$ as benzenoid structures become more strictly peri-condensed, they become relatively more preferred from a thermodynamic point of view. Furthermore, among the cata-condensed PAH6 structures, the total resonant sextet isomers are the most stable ones. For example, triphenylene is more stable than any of its 4 other $C_{18}H_{12}$ isomers [31]. Similarly *2*, *8*, and *29–31* are predicted to be more stable than any of their 122, 445 and 1686 other $C_{30}H_{18}$, $C_{42}H_{24}$ and $C_{54}H_{30}$ isomers, respectively [33]. Thus among the more than $10^4$ benzenoid hydrocarbons having their number of formula carbons divisible by six, the 60 minimally strained total resonant sextet isomers shown in Fig. 1 have the greatest relative likelihood of being formed under random pyrolytic conditions [34].

The data in Table 4 can be recast into $\Delta G_f^0(298)/N_c$ which gives the standard free energy of formation per carbon atom for gaseous benzenoid hydrocarbons. For acenes $N_H = 2(r-1) + 6$, $N_c = 4(r-1) + 6$ and $N_{pc} = 2(r-1)$ where $r$ is the number of acene rings. Using these relationships, $\text{limit}_{r \to \infty}$ $(\Delta G_f^0/N_c) = 3.0767$ kcal mol$^{-1}$ per carbon atom for the infinite acene structure. Similarly, for the graphite-like strictly peri-condensed polycircumcoronene series $N_H = 6(n+1)$, $N_c = 6(n+1)^2$, $N_{pc} = 6n$ and $N_{Ic} = 6n^2$ where $n = 1$ for coronene ($C_{24}H_{18}$), $n = 2$ for circumcoronene ($C_{54}H_{18}$), $n = 3$ for dicircumcoronene, etc. Using these relationships, $\text{limit}_{n \to \infty}$ $(\Delta G_f^0/N_c) = 0.9075$ kcal mol$^{-1}$ per carbon atom for infinite graphite. These results again demonstrate that for a given $N_c$ strictly peri-condensed benzenoids are more stable. It should be noted that this latter value (0.9075 kcal mol$^{-1}$ per carbon atom) is the standard free energy of graphite in the hypothetical gaseous state and not the atomized state for which $\Delta G_f^0(298) = 160.85$ kcal mol$^{-1}$ per carbon atom. For triphenylene $\Delta G_f^0(298)/N_c = 1.698$ kcal mol$^{-1}$ per carbon atom, and Table 5 presents additional standard free energy of formation values for *1* to *60*. From these data, one can conclude that there is a thermodynamic preference for the larger and more highly condensed polycyclic aromatic hydrocarbon molecule.

## CONCLUSIONS

The analytical methodology for identifying larger benzenoid hydrocarbons of pyrolytic origin is evolving, and it is predicted that total resonant sextet isomers are thermodynamically preferred [6–10,21,22]. The Benson group additivity method for computing thermodynamic quantities are graph theoretically based [31,32]. Enumeration of many of the total resonant sextet benzenoids with their Hückel molecular orbital and thermodynamic parameters has been accomplished for the first time, and the resonant sextet concept has been reviewed. The recent work of Stein and Brown has shown that total resonant sextets which are also strictly peri-condensed (like *14*) represents the most stable class of benzenoid hydrocarbons possible [35]. High temperature products are usually the thermodynamic products.

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