

# Is 2-D Graphite an Ultimate Large Hydrocarbon? 1. Energy Spectra of Giant Polycyclic Aromatic Hydrocarbons

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The energy spectra of three classes of polybenzenoid hydrocarbons with a large number  $N$  ( $N \approx 10^3$ ) of carbon atoms have been studied theoretically. It is shown that in the asymptotic case  $N \rightarrow \infty$  the energy gap (EG)  $\Delta E(N \rightarrow \infty)$  is different from zero if the electron correlation is taken into account; that is, the  $\pi$  systems calculated should possess semiconductor properties. The results for the  $\Delta E(N \rightarrow \infty) \neq 0$  of the hydrocarbons are in qualitative agreement with the results calculated for the EG of three classes of 1-D ladder polymers, which can be considered as models of quasi-1-D graphite. With increasing width ( $L$ ) of the polymers, the band gap  $\Delta E(L \rightarrow \infty)$  approaches a value different from zero. The problem of the existence of defect states of hydrocarbons with vacancies is briefly discussed.

## 1. Introduction

Extremely large polycyclic aromatic hydrocarbons (PAHs) are of interest as potential materials for optoelectronics<sup>1–3</sup> and molecular electronics.<sup>4,5</sup> With the synthesis of special PAHs, “superconerones”,<sup>6</sup> the prospect for the practical application of PAHs in molecular electronics is very realistic. In a recent paper,<sup>4</sup> it has been shown that single molecules of large PAHs (in the special case of ref 4, alkyl-substituted peri-condensed hexabenzocoronene adsorbed on graphite) can have diodelike properties.

The structure and energy spectra of PAHs are also of theoretical interest as molecular subunits of graphite, the latter representing an “ultimate large aromatic molecule”.<sup>7</sup> Various models are referred to when theoretically describing 2-D graphite; when the Born-von Karman cyclic conditions are fulfilled, graphite adopts the shape of a torus<sup>8</sup> (see also the papers of Klein<sup>9,10</sup> for other symmetrical forms of 2-D graphite), a form that is obviously unknown. Similar to 2-D graphite, for which the cyclic conditions are fulfilled, are the carbon nanotubes<sup>11</sup> (for theoretical papers see also ref 12 and references given therein). However, in this case, there are edge effects. In a recent paper, Liu et al.<sup>13</sup> have observed experimentally single-wall carbon nanotubes that are perfect tori. Another model of 2-D graphite is that of polycondensed ladder-type quasi-1-D  $\pi$ -polymers with one translation period for which the width  $L$  goes to  $\infty$ . The 2-D layers of the synthetic and natural graphite are clusters of a few hundreds or a few thousands of carbon atoms.<sup>14</sup> However, the physical nature of the structure of the ledges is unknown.

The first theoretical investigations of PAHs as models of graphite have been carried out by Coulson<sup>15</sup> in the Hückel approximation, and the terms “1-D graphite” and “graphite crystallites” have been introduced (see also the earlier paper of Rajanow<sup>16</sup>). Thereafter, PAHs have been studied theoretically

by various authors (see the review<sup>17</sup> and the papers<sup>18,19</sup> and references given therein). The first theoretical study of hexagonal structures in nature was carried out by J. Kepler.<sup>20</sup>

The most important energy characteristic of a many-electron  $\pi$  system, in particular of a PAH or 1(2)-D graphite, is the energy gap (EG). Real homonuclear alternant 1-D  $\pi$  systems with an energy gap  $\Delta E = 0$  are unknown up to now. This suggests the following principal question: do alternant 1-D systems with a zero energy gap exist? In a series of papers (see refs 21–25 and references given therein), a large number of alternant 1-D  $\pi$  systems have been investigated theoretically and numerically. In all cases, the calculated value of  $\Delta E$  were greater than 0 when taking into account electron correlation. It could be shown analytically<sup>22</sup> that the EG of an arbitrary homonuclear alternant system with a singlet (closed shell) ground state is different from zero; that is, the ground state of a regular alternant 1-D  $\pi$  system (polymer) is always a dielectric one. This result is in agreement with the experimental finding<sup>4,6</sup> that PAHs of different topologies having a large number of  $\pi$  centers show longest wavelength absorptions in the NIR region, i.e., their energy gap is greater than 0. It might be mentioned in this context that Stein and Brown<sup>18,19</sup> have stated in their important papers on  $\pi$ -electron properties of large polycyclic aromatic hydrocarbons “. . . we also did similar calculations using a SCF version of MO theory. . . . Unfortunately, in the graphite limit, it yielded a nonzero band gap”.

The above considerations have prompted us to investigate the energy spectra of very large PAHs and to compare the results with those of 1(2)-D models of graphite. This study is closely related to the occurrence of surface (defect) states in graphite, graphite crystalites, and 1(2)-D graphites. The presence of different types of defects in a crystal leads to the existence of one or more surface states and changes its energy spectra as well as many physical and chemical properties.<sup>26,27</sup> Of specific interest are localized states whose energy levels lie in the forbidden energy regions, in particular in the EG.<sup>28</sup> Typical examples of crystal defects are vacancies, topological defects, and substitution of one or more H atoms by atoms or groups

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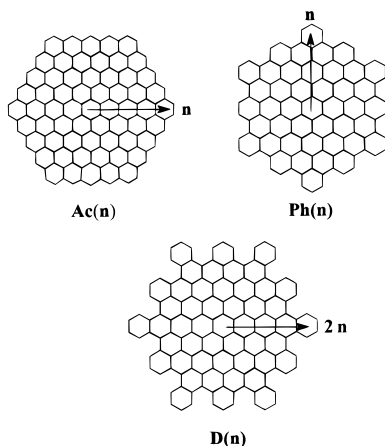
that form new  $\pi$  bonds.<sup>26,27,29</sup> These defects determine the different types of surface states such as Shockley, Tamm, or chemisorption states.<sup>29</sup> General conditions for the existence or nonexistence of surface states in a 2-D infinite graphite crystal with Born–Karman conditions were studied by Koutecky.<sup>29</sup> Graphitic polymer stripes with surface (edge) states were investigated in a recent paper by Klein.<sup>30</sup> Fujita et al.<sup>31</sup> have considered localized states at graphite edges caused by different edge shapes.

In this first communication of the series, we consider the influence of the various contributions to the EG of some classes of large PAHs and 1(2)-D graphite models.

The study of the influence of different types of defects on the energy spectra of the PAHs and 1(2)-D graphites is another objective of the present work. Studying the energy spectra of PAHs and 1(2)-D graphites with different defects requires a nontrivial extension of the theoretical methods used herein (see below). Therefore, systems with defect states are only briefly discussed by giving a few examples.

## 2. Models of the Homologous Hydrocarbons and 1-D Graphite

The calculations were carried out for three homologous series of hydrocarbons with  $D_{6h}$  symmetry: **Ac**(*n*), **Ph**(*n*), and **D**(*n*), with a number of  $\pi$  centers  $N \leq 2400$ .



The number of  $\pi$  centers,  $N$ , of the homologous hydrocarbons are given by the following formulas:

$$\mathbf{Ac}(n) \ (n = 0 \text{ (benzene)}, 1-19) \ N = 6(1 + n^2)$$

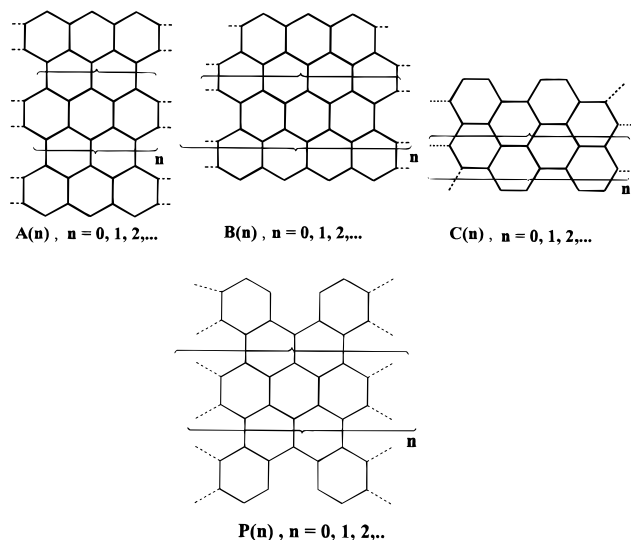
$$\mathbf{Ph}(n) \ (n = 0 \text{ (benzene)}, 1-11) \ N = 6(1 + 3n + 3n^2)$$

$$\mathbf{D}(n) \ (n = 0 \text{ (benzene)}, 1-9) \ N = 6(1 + 3n + 4n^2)$$

Within the Hückel MO (HMO) method, the energetic characteristics and reactivity indices of the same models ( $N < 2300$ ) have been calculated in the papers of Stein and Brown.<sup>18,19</sup>

In the HMO approximation, the energy gap in the spectra of one-particle excitations,  $\Delta E$  of the **Ac**(*n*) and **D**(*n*) hydrocarbons, tends monotonically to zero,<sup>18,19</sup> a value which coincides with the one calculated by means of the  $\pi$ -band HMO model of graphite.<sup>8</sup> In the case of **Ph**(*n*) hydrocarbons,  $\Delta E$  tends monotonically, however very slowly, to a value of  $\sim 0$  (see also Table 3).<sup>18,19</sup>

Except for these hydrocarbons, we consider also the energy spectra of the infinite quasi-1-D polymers **A**(*n*), **B**(*n*), **C**(*n*), and **P**(*n*):



Polymers **A**(*n*) and **B**(*n*) have the same edge structure (polyacene type) as the PAHs **Ac**(*n*). Polymers **C**(*n*) are characterized by a polyphenanthrene-like edge structure. Polymers **P**(*n*) have the same edge structure like **D**(*n*). The energy spectra of the **A**(*n*), **B**(*n*), and **C**(*n*) polymers have been studied already,<sup>23</sup> however without optimized geometries (with the extended SSH method, see Section 3) of the polymer models and with nonstandard parameters (see Table 5).

The polymers are assumed to be 1-D systems for which the Born–Karman conditions are fulfilled. The method described in ref 32 also allows one to treat polymers with a finite number of monomeric units. In this case, the polymer is thought to be embedded in a cylindrical surface exhibiting at least  $C_N$  symmetry ( $D_{(2m)h}$  in the case of the **A**(*n*) and **P**(*n*) polymers, and  $D_{(2m)d}$  for the **B**(*n*) and **C**(*n*) polymers, when all bond lengths are equal), where  $\omega_k = 2\pi k/N$ ,  $\omega_k \in [-\pi, \pi]$  denotes the arguments of the character of rotation in the irreducible representation  $\Gamma_k$  of the corresponding symmetry group.

## 3. Methods of Investigations

**Band Gap Equation of Alternant  $\pi$ -Electron Systems.** As the investigated hydrocarbons are alternant  $\pi$  systems, their energy spectra can be calculated by means of the AMO (alternant molecular orbitals) version of the extended HF method (EHF).<sup>33</sup> It has been shown that the EG of an arbitrary homonuclear alternant system having a singlet ground state is given by the formula<sup>34</sup>

$$\Delta E(\text{EHF}) = (\Delta_{\text{corr}}^2 + \Delta E(\text{HF})^2)^{1/2} \quad (1)$$

In the Hubbard approximation,<sup>35</sup> eq 1 obtains the form

$$(\Delta_{\text{corr}}^2 + (\Delta_{\text{top}} + \Delta_{\text{geom}})^2)^{1/2} \quad (2)$$

where  $\Delta_{\text{corr}}$  is the correlation correction,  $\Delta_{\text{top}}$  is the EG in the “topological” approximation, that is, in the case that all bond lengths of the system are equal and all resonance integrals  $\beta$  between adjacent  $\pi$  centers are equal. The sum  $\Delta_{\text{top}} + \Delta_{\text{geom}}$  expresses the EG calculated when taking into account the bond length distortion.

The correlation correction of EG is given by  $\Delta_{\text{corr}} = 2\delta\gamma$ , where  $\gamma$  is the one-center Coulomb repulsion integral (Hubbard parameter<sup>32</sup>) of the carbon  $\pi$  centers. The dimensionless correlation parameter  $\delta$  satisfies the equation

$$M\delta = \delta \sum_k \gamma/(\delta^2\gamma^2 + \beta^2 e_k^2)^{1/2} \quad (3)$$

where  $M$  is the number of the  $\pi$  centers and  $e_k$  is the MO energies. Equation 3 has always a trivial solution  $\delta = 0$ ; that is, the AMO energies coincide with the energies obtained in the one-electron HMO approximation. If  $\delta \neq 0$ , eq 3 takes the form

$$M = \sum_k \gamma/(\delta^2\gamma^2 + \beta^2 e_k^2)^{1/2} \quad (4)$$

From the inequality

$$1 = 1/M \sum_k \gamma/(\delta^2\gamma^2 + \beta^2 e_k^2)^{1/2} < 1/M \sum_k \gamma/|\beta e_k|$$

there follows the self-consistency condition

$$|\beta/\gamma| < (|\beta/\gamma|)_{\text{crit}} = 1/M \sum_k \gamma/|e_k| \quad (5)$$

That is, if the condition of eq 5 is not fulfilled, eq 3 has no solution  $\delta \neq 0$ .

The MO energies  $e_k$  (and the topological and geometrical components of EG) in eq 4 were calculated using the HMO method by the numerical diagonalization of the corresponding matrix. If we adopt for the polymers a Bloch form of the wave vector  $\omega_k \in [-\pi, \pi]$ , the MO energies  $e(\omega_k)$  are obtained by the numerical diagonalization of the matrix<sup>32</sup>

$$\mathbf{E}(k) = \mathbf{E}_0 + \mathbf{V} \exp(i\omega_k) + \mathbf{V}^+ \exp(-i\omega_k) \quad (6)$$

where  $\mathbf{E}_0$  is the energy matrix of the EU,  $\mathbf{V}$  is the interaction matrix between neighboring elementary units (EUs) ( $\mu$ -th and  $(\mu + 1)$ -th), and  $\mathbf{V}^+$  is the transposed matrix. The numerical results were obtained with the following set of standard parameters:  $\beta = -2.4$  eV,  $\gamma = 5.4$  eV,  $\beta/\gamma = 0.44444$ . These parameter values have been extensively employed for the description of the EG of many homonuclear  $\pi$ -electron systems for which  $\Delta E$  is experimentally known. Using these parameters, quite reasonable results could be achieved.<sup>21,22, 33–35</sup>

**Geometry of the Hydrocarbons and Infinite Polymers.** To estimate the geometry of the infinite polymers, an extended Su–Schrieffer–Heeger (SSH) model<sup>36</sup> was used. This approach, the SSH-PPP model,<sup>37</sup> incorporates the linear electron–lattice coupling and a harmonic bond-strain potential as described in the SSH model and the  $\pi$ -electron–electron interaction corresponding to the Pariser–Parr–Pople (PPP) approximation.<sup>38</sup> The following parametrization was used: the electron–lattice coupling constant  $\alpha = 3.21$  eV/Å and the spring constant  $K = 24.6$  eV/Å<sup>2</sup>.<sup>37</sup>

For the two-center Coulomb repulsion integrals  $\gamma_{ij}$  (to calculate the energy of the electron–electron interaction), the screened Mataga–Nishimoto approximation<sup>39</sup> was used ( $\gamma_0 = 10.84$  eV).

$$\gamma_{ij} = e^2/(e^2/\gamma_0 + DR_{ij}) \quad (7)$$

The equilibrium geometry of the hydrocarbons **Ac**( $n$ ) ( $n = 1, 2, 3, 4$ ) was calculated by means of the AM1 method.<sup>40,41</sup> For the calculation of the geometrical component of EG,  $\Delta_{\text{geom}}$  in eq 2, the dependence of the resonance integrals between the neighboring carbon atoms on the bond lengths  $R$  was calculated

**TABLE 1: Dependence of the Energy Gap  $\Delta E$  and the Components  $\Delta_{\text{top}}$  and  $\Delta_{\text{corr}}$  to  $\Delta E$  (All Entries Are in eV) on the Number  $N$  of  $\pi$  Centers in the Homologous Hydrocarbons **Ac**( $n$ )**

$n$	$N$	$\Delta_{\text{top}}$	$\delta$	$\Delta_{\text{corr}}$	$\Delta E$
1	24	2.588	$a$		2.588 <sup>b</sup>
2	54	1.642	0.083 65	0.903	1.874
3	96	1.101	0.097 21	1.050	1.522
4	150	0.752	0.100 43	1.085	1.320
5	216	0.514	0.099 76	1.077	1.194
6	294	0.349	0.097 68	1.055	1.111
7	384	0.234	0.095 19	1.028	1.054
8	486	0.155	0.092 67	1.001	1.013
9	600	0.102	0.090 24	0.975	0.980
10	726	0.065	0.087 95	0.950	0.952
11	864	0.042	0.085 80	0.927	0.928
17	1944	0.002	0.075 59	0.816	0.816
18	2166	0.0015	0.074 24	0.802	0.802
19	2400	0.001	0.073 10	0.790	0.790
$\infty$	$\infty$	0			0.718 <sup>c</sup>
$\infty$	$\infty$				0.740 <sup>d</sup>

<sup>a</sup> Equation 3 has no solution  $\delta \neq 0$ . <sup>b</sup>  $\Delta E_{\text{exp}} = 3.00$  eV.<sup>54</sup> <sup>c</sup> Value calculated by means of Aitken's formula, three-point Pade approximation<sup>53</sup> using the last three values ( $n = 17–19$ ). <sup>d</sup> Calculated by means of the interpolation formula ( $n \geq 5$ )  $\Delta E(n) = 0.740 + 0.7238 e^{-0.1228 n}$ .

**TABLE 2: Energy Gap Components  $\Delta_{\text{top}}$ ,  $\Delta_{\text{geom}}$ , and  $\Delta_{\text{corr}}$  (All Entries Are in eV) in Dependence on the Number  $N$  of  $\pi$  Centers in the Homologous Hydrocarbons **Ac**( $n$ )**

$n$	$N$	$\Delta_{\text{top}}$	$\Delta_{\text{geom}}$	$\Delta_{\text{corr}}$	$\Delta E$
1	24	2.588	0.105	$a$	2.693
2	54	1.642	0.134	0.076 51	1.959
3	96	1.101	0.127	0.089 02	1.559
4	150	0.752	0.090	0.091 71	1.301
$\infty$	$\infty$	0			0.842 <sup>b</sup>

<sup>a</sup> Equation 3 has no solution  $\delta \neq 0$ . <sup>b</sup> Value calculated by means of Aitken's formula, three-point Pade approximation<sup>53</sup> using the last three values ( $n = 2–4$ ).

with Mulliken's formula,<sup>42</sup>

$$\beta(R) = \beta_0 S(R)/S(R_0),$$

where the  $S$  are the overlap integrals (calculated with  $R_0 = 1.4$  Å and  $Z_C = 3.25$ ).

#### 4. Numerical Results and Discussion

**Energy Spectra of the Hydrocarbons.** In Table 1 are collected the results of the band gap components ( $\Delta_{\text{top}}$  and  $\Delta_{\text{corr}}$ ) of hydrocarbons **Ac**( $n$ ). The calculated values of  $\Delta E(n)$  tend monotonically to a value different from zero. The nonzero energy gap,  $\Delta E(\infty) \approx 0.7$  eV, is caused only by the correlation correction and  $\Delta E(\infty) = \Delta_{\text{corr}}$ . The results in Table 1 were obtained with ideal geometries, i.e., without the geometrical contribution  $\Delta_{\text{geom}}$ . In Table 2 are given the values of the geometrical components of the EG for the first four members of hydrocarbons **Ac**( $n$ ),  $n = 1–4$ , calculated with a geometry obtained by means of AM1 method. The geometrical component is small and on the order of magnitude of 0.1 eV. This means that, in the asymptotic case  $n \rightarrow \infty$ ,  $\Delta_{\text{corr}}$  is the main component of the nonzero energy gap. However,  $\Delta_{\text{corr}}$  depends indirectly on the geometry of the  $\pi$  systems when the MO energies  $e_k$  obtained with real geometry were used in eq 4.

In Table 3 are collected the results of the band gap components ( $\Delta_{\text{top}}$  and  $\Delta_{\text{corr}}$ ) of the hydrocarbons **Ph**( $n$ ). In the HMO approximation,  $\Delta E$  tends monotonically, however slowly, to a value of  $\sim 0.2$  eV. The results for the hydrocarbons **D**( $n$ ), calculated with ideal geometry are given in Table 4. In all cases,

**TABLE 3: Dependence of Energy Gap  $\Delta E$  and the Components  $\Delta_{\text{top}}$  and  $\Delta_{\text{corr}}$  (All Entries Are in eV) on the Number  $N$  of  $\pi$  Centers of the Hydrocarbons Ph( $n$ )**

$n$	$N$	$\Delta_{\text{top}}$	$\delta$	$\Delta_{\text{corr}}$	$\Delta E$
1	42	2.231	$a$	0	2.231 <sup>b</sup>
2	114	1.397	0.0122	0.132	1.404
3	222	1.014	0.0216	0.234	1.040
4	366	0.795	0.0225	0.243	0.831
5	546	0.654	0.0221	0.240	0.696
6	762	0.555	0.0214	0.231	0.601
9	1626	0.381	0.0192	0.207	0.433
10	1986	0.345	0.0186	0.201	0.399
11	2382	0.316	0.0181	0.195	0.371
$\infty$		0.196 <sup>c</sup>			0.240 <sup>c</sup>
$\infty$		0.196 <sup>d</sup>			0.240 <sup>e</sup>

<sup>a</sup> Equation 3 has no solution  $\delta \neq 0$ . <sup>b</sup>  $\Delta E_{\text{exp}} = 2.40$  eV.<sup>55</sup> <sup>c</sup> Values calculated by means of Aitken's formula, three-point Pade approximation<sup>53</sup> using the last three values of  $\Delta_{\text{top}}$  and  $\Delta E$ , respectively ( $n = 9-11$ ). <sup>d</sup> Value calculated by means of the equation  $\Delta E(n) = 0.196 + 1.2960 e^{-0.2162n}$  ( $n \geq 5$ ). <sup>e</sup> Value calculated by means of the equation  $\Delta E(n) = 0.240 + 1.1053 e^{-0.1942n}$  ( $n \geq 5$ ).

**TABLE 4: Dependence of Energy Gap  $\Delta E$  and the Components  $\Delta_{\text{top}}$  and  $\Delta_{\text{corr}}$  (All Entries Are in eV) on the Number  $N$  of  $\pi$  Centers of the Hydrocarbons D( $n$ )**

$n$	$N$	$\Delta_{\text{top}}$	$\delta$	$\Delta_{\text{corr}}$	$\Delta E$
1	48	2.160	$a$	0	2.160
2	138	1.156	0.062 59	0.676	1.339
3	276	0.686	0.066 83	0.724	0.995
7	1308	0.095	0.096 54	0.615	0.622
8	1686	0.056	0.054 77	0.592	0.594
9	2112	0.032	0.052 85	0.571	0.572
$\infty$		$\sim 0^b$			0.484 <sup>b</sup>
$\infty$					0.491 <sup>c</sup>

<sup>a</sup> Equation 3 has no solution  $\delta \neq 0$ . <sup>b</sup> Values calculated by means of Aitken's formula, three-point Pade approximation<sup>53</sup> using the last three values of  $\Delta_{\text{top}}$  and  $\Delta E$ , respectively ( $n = 7-9$ ). <sup>c</sup> Value calculated by means of the equation  $\Delta E(n) = 0.491 + 0.7074 e^{-0.2411n}$ .

**TABLE 5: Calculated Values of the Correlation Parameter  $\delta$  and the Corresponding Values of EG ( $\Delta E = \Delta_{\text{corr}}$ , in eV) of the Hydrocarbon Ac(19) (see Table 1) for Different Values of the Parameter  $|\beta/\gamma|$** 

$ \beta/\gamma ^a$	$\delta$	$\Delta_{\text{corr}}$
0.420 00	0.102 08	1.110
0.425 00	0.095 57	1.032
0.442 48	0.075 19	0.812
0.430 00	0.089 33	0.965
0.440 00	0.077 82	0.841
0.444 44	0.073 17	0.790
0.450 00	0.067 73	0.731
0.455 00	0.063 25	0.683
0.468 50 <sup>b</sup>	0.052 85	0.571

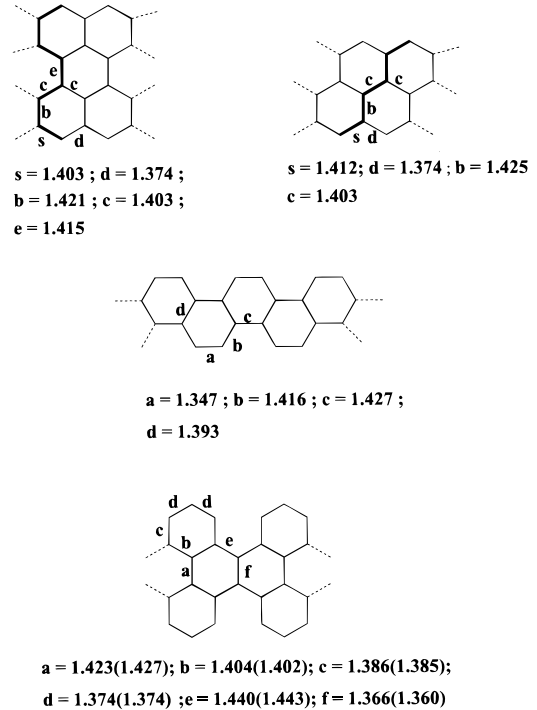
<sup>a</sup> Calculated with  $\gamma = 5.4$  eV. <sup>b</sup> Value used in ref 25.

the extrapolated values ( $n \rightarrow \infty$ ) of EG are different from zero and mainly determined by the electron correlation. Hence, these  $\pi$  systems should possess semiconductor properties.

These new qualitative results were obtained in the Hubbard approximation with a given parametrization,  $|\beta/\gamma| = 0.44444$ . The values of the correlation component,  $\Delta_{\text{corr}}$ , depend on the ratio  $|\beta/\gamma|$ . From eq 4, it follows that the correlation correction  $\delta$  and the ratio  $C = |\beta/\gamma|$  are connected with eq 8,

$$\sum_k 1/(\delta_1^2 + C_1^2 e_k^2)^{1/2} = \sum_k 1/(\delta_2^2 + C_2^2 e_k^2)^{1/2} \quad (8)$$

as it is shown in Table 5. The quantitatively different results, however, do not change the qualitative results, namely, a nonzero value of the EG.



**Figure 1.** Equilibrium geometries of the polymers **A(0)**, **B(0)**, **C(0)**, and **P(0)** obtained by means of the SSH-PPP method (bond lengths in angstroms). The calculations start from the undistorted lattice (all bond lengths = 1.4 Å). The numerical values of the bond lengths were obtained with a screening parameter  $D = 3$  (see eq 7). The values in brackets for polymer **P(0)** are obtained with  $D = 1$ .

**TABLE 6: Dependence of the Energy Gap  $\Delta E = \Delta_{\text{corr}}$  (in eV) on the Number  $n$  of the Polymers **A(n)** and **B(n)****

$n$	$\delta$	$\Delta E$ <b>A(n)</b>	$\delta$	$\Delta E$ <b>B(n)</b>
0	0.1437	1.555	0.161 51	1.744
1	0.1262	1.363	0.135 32	1.461
2	0.1130	1.220	0.119 20	1.287
3	0.1035	1.118	0.108 09	1.168
4	0.0965	1.042	0.099 87	1.079
5	0.0907	0.980	0.093 43	1.009
6	0.0860	0.929	0.088 28	0.953
7	0.0821	0.887	0.083 92	0.906
8	0.0787	0.850	0.080 16	0.867
9	0.0757	0.818	0.077 22	0.834
$\infty$		0.612 <sup>a</sup>		0.653 <sup>a</sup>
$\infty$		0.613 <sup>b</sup>		0.653 <sup>c</sup>

<sup>a</sup> Values calculated by means of Aitken's formula,<sup>53</sup> three-point Pade approximation using the last three values of  $\Delta E$  ( $n = 7-9$ ). <sup>b</sup> Value calculated by means of the equation  $\Delta E(n) = 0.6132 + 0.75649 e^{-0.14518n}$ . <sup>c</sup> Value calculated by means of the equation  $\Delta E(n) = 0.6525 + 0.81624 e^{-0.16705n}$ .

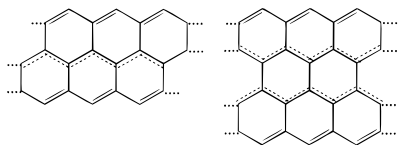
**Energy Spectra of the Polymers.** The values of EG for the polymers were calculated with a geometry obtained using the SSH-PPP model. The equilibrium geometries of polymers **A(0)**, **B(0)**, **C(0)**, and **P(0)** are shown in Figure 1.

The bond length distortions for the polymers are connected with a decrease of the ground-state energy. In relation to the undistorted lattice, the energy lowering per  $\pi$  center,  $\Delta\epsilon$ , is 7.0 meV for polymer **A(0)** and 4.4 meV for polymer **B(0)**. The numerical results were obtained with  $D = 3$  in eq 7. The energy lowering of polymers **C(n)** is given in Table 7.

In Table 6, the calculated values of EG of the **A(n)** and **B(n)** polymers are documented. The numerical results show that for all **A(n)** and **B(n)** polymers  $\Delta_{\text{geom}}$  is very small or zero. Because the topology component is also equal to zero, EG for the polymers **A( $\infty$ )** and **B( $\infty$ )** is determined only by the electron



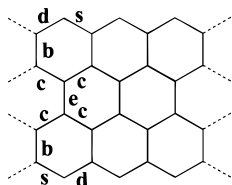
correlation;  $\Delta E = \Delta_{\text{corr}}$ . With respect to the undistorted lattice, the bond length distortions occur mainly in the periphery of the polymers (see Figure 1). Qualitatively, the results for the bond length distortions correspond to the structures shown below.



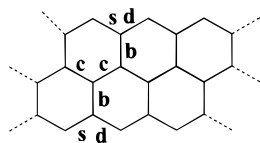
The absence of the geometrical component of EG is a structural peculiarity of the **A**(*n*) and **B**(*n*) polymers. It is possible to show qualitatively that the geometrical component of the polymers is zero or tends toward zero using the polynomial representation of the eigenvalue problem of eq 6. The characteristic polynomial (see eq 6)

$$\det \mathbf{E} = x^{2m} + a_{m-2}x^{2m-2} + a_2x^2 + a_0 = 0 \quad (9)$$

( $x = e(k)/\beta$ ) of the **A**(0) and **B**(0) polymers has the form (see Figure 1)



$$a_0[\mathbf{A}(0)] = c^4 \{ (d^2 + c^2)(6 + 8 \cos k + 2 \cos(2k)) + (d^3s + ds^3)(16 + 28 \cos k + 16 \cos(2k) + 4 \cos(3k)) + d^2s^2(26 + 40 \cos k + 20 \cos(2k) + 8 \cos(3k) + 2 \cos(4k)) \} \quad (10)$$



$$a_0[\mathbf{B}(0)] = 2c^2 \{ (d^4 + s^4)(1 + \cos k) + 2(d^3s + ds^3)(1 + 2 \cos k + \cos(2k)) + 2d^2s^2(4 + 5 \cos k + 2 \cos(2k) + \cos(3k)) \} \quad (11)$$

In eqs 10 and 11, *d*, *s*, *b*, and *c* denote the ratios between the resonance integrals:  $d = \beta_d/\beta$ ,  $s = \beta_s/\beta$ , etc. If  $k = \pi$ ,  $a_0[\mathbf{A}(0)] = a_0[\mathbf{B}(0)] = 0$ . Hence, the characteristic polynomials (eqs 10 and 11) have a root  $x = 0$ . Since the root  $x = 0$  occurs twice (see eq 9), it follows that the sum

$$\Delta_{\text{top}} + \Delta_{\text{geom}} = 0$$

It should be emphasized that the values of  $a_0[\mathbf{A}(0)]$  and  $a_0[\mathbf{B}(0)]$  at  $k = \pi$  (eqs 10 and 11) do not depend on the bond length of the bonds *b* and *c*; that is, the sum  $\Delta_{\text{top}} + \Delta_{\text{geom}} = 0$  at an arbitrary distortion of the bonds *b* and *c*.

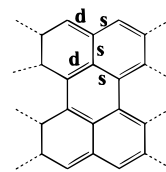
The geometrical component of EG,  $\Delta_{\text{geom}}$ , is different from zero, assuming a bond length alternation not only in the periphery but also in the central part of the polymers. However,  $\Delta_{\text{geom}}$  is very small. For instance, the characteristic polynomial of the polymer **A**(0) with the following bond lengths alternation

**TABLE 7: Oscillation of the Energy Gap  $\Delta E$  and the Components  $\Delta_{\text{top}}$ ,  $\Delta_{\text{geom}}$ , and  $\Delta_{\text{corr}}$  (All Entries Are in eV) with the Number *N* of  $\pi$  Centers in the EU of Polymers **C**(*n*)**

<i>N</i>	<i>n</i>	type	$\Delta_{\text{top}}$	$\Delta_{\text{geom}}$	$\Delta_{\text{corr}}$	$\Delta E$	$\Delta \epsilon^a$
8	0	3 <i>p</i>	1.834	0.342	<i>b</i>	2.176	6.35
12	1	3 <i>p</i> + 1	1.185	0.170	<i>b</i>	1.356	4.51
16	2	3 <i>p</i> + 2	0	0.136	0.718	0.731	3.89
20	3	3 <i>p</i>	0.812	0.074	0	0.886	2.94
24	4	3 <i>p</i> + 1	0.653	0.050	0	0.703	2.64
28	5	3 <i>p</i> + 2	0	0.044	0.415	0.417	2.39
32	6	3 <i>p</i>	0.522	0.019	0	0.541	2.0
36	7	3 <i>p</i> + 1	0.452	0.015	0	0.467	1.9
40	8	3 <i>p</i> + 2	0	0.011	0.371	0.372	1.6
$\infty^c$		3 <i>p</i>				0.452	
$\infty^c$		3 <i>p</i> + 1				0.333	
$\infty^c$		3 <i>p</i> + 2				0.364	

<sup>a</sup> Energy lowering per  $\pi$  center determined by the geometry optimization by means of the SSH–PPP method. The numerical results were obtained with  $D = 3$  in eq 7. <sup>b</sup> Equation 3 has no solution  $\delta \neq 0$ . <sup>c</sup> Values calculated by means of Aitken's formula, three-point Padé approximation.<sup>53</sup>

(the repeat unit is kept with  $C_{2v}$  symmetry) reads



$$a_0 = d^8 + 8d^7s \cos k + 4d^6s^2(4 + 3 \cos(2k)) + 8d^5s^3(6 \cos k + \cos(3k)) + 2d^4s^4(18 + 16 \cos(2k) + \cos(4k)) + 8d^3s^5(6 \cos k + \cos(3k)) + 4d^2s^6(4 + 3 \cos(2k)) + 8ds^7 \cos k + s^8$$

When  $k = \pi$ ,  $a_0 = (d - s)^8$ .  $(d - s)^8$  is a small quantity tending to zero; that is,  $a_0$  goes to 0. For instance, if we assume the following strong alternation in the bond lengths,  $R_s = 1.45 \text{ \AA}$  and

$$R_d = 1.35 \text{ \AA}, \text{ then } d = 1.087, s = 0.91, \text{ and } (d - s)^8 = 0.168^8 < 10^{-5}.$$

Qualitatively, the results for the bond length distortions of polymer **C**(0) correspond to the structure

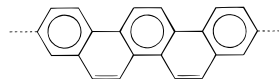
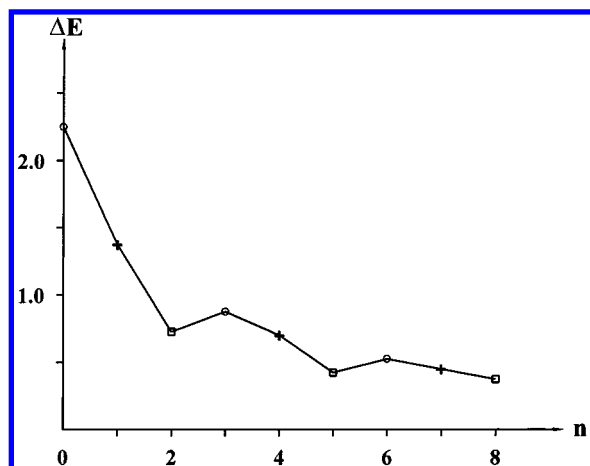


Table 7 presents the calculated values of EG of **C**(*n*) polymers. The topological component of EG was calculated using the analytical expression for the MO energies given in the paper of Klein.<sup>43</sup> In the HMO approximation, the **C**(*n*) polymers split into two groups.<sup>43</sup> For **C**(*n*) polymers with  $n = 3p + 2$  ( $p = 0, 1, 2, \dots$ ), the topological component  $\Delta_{\text{top}} = 0$ . For **C**(*n*) polymers with  $n = 3p$  ( $p = 1, 2, 3, \dots$ ) and  $n = 3p + 1$  ( $p = 0, 1, 2, \dots$ ),  $\Delta_{\text{top}} \neq 0$  (see Table 7).

Taking into account the electron correlation leads to a significant correction of EG. The values of  $\Delta E(n)$  do not decrease monotonically (see Figure 2). The values decrease monotonically for each of the three groups of **C**(*n*), the  $3p$ ,  $3p + 1$ , and  $3p + 2$  series. Qualitatively, the same results were obtained in a recent paper of Yoshizawa et al.,<sup>44</sup> using the fragment MO method. However, "with an increase in width of the polymers, the band gap approaches zero".<sup>44</sup> As can be



**Figure 2.** Oscillation of energy gap  $\Delta E$  (in eV) of the different types of polymers  $C(n)$  as a function of  $n$ :  $\circ$ , type  $3p$ ;  $+$ , type  $3p + 1$ ;  $\square$ , type  $3p + 2$ .

**TABLE 8: Dependence of the Energy Gap  $\Delta E$  and the Components  $\Delta_{\text{top}}$ ,  $\Delta_{\text{geom}}$ , and  $\Delta_{\text{corr}}$  (All Entries Are in eV) on the Number  $N$  of  $\pi$  Centers in the EU for Polymers  $D(n)$**

$n$	$N$	$\Delta_{\text{top}}$	$\Delta_{\text{geom}}$	$\Delta_{\text{corr}}$	$\Delta E$
2	14	1.494	0.248	$a$	1.742
3	22	0.646	0.154	0.721	1.077
4	30	0.308	0.084	0.787	0.877
5	38	0.152	0.060	0.743	0.772
6	46	0.076	0.047	0.731	0.741
$\infty^b$					0.728

<sup>a</sup> Equation 3 has no solution  $\delta \neq 0$ . <sup>b</sup> Value calculated by means of Aitken's formula, three-point Pade approximation<sup>53</sup> using the last three values ( $n = 4-6$ ).

seen from Table 7, the extrapolated values ( $n \rightarrow \infty$ ) of the width of EG are different from zero for each of the three groups of  $C(n)$ .

The energy gap components of polymers  $P(n)$  are given in Table 8. The geometrical component of EG was calculated using the equilibrium geometry obtained by means of the SSH-PPP method. At  $n \geq 4$ , the main contribution to the energy gap is  $\Delta_{\text{corr}}$ .

Thus, in all cases of the hydrocarbons and the polymers, the extrapolated values ( $n \rightarrow \infty$ ) of EG are different from zero and mainly determined by the electron correlation. Hence, these  $\pi$  systems should possess semiconductor properties.

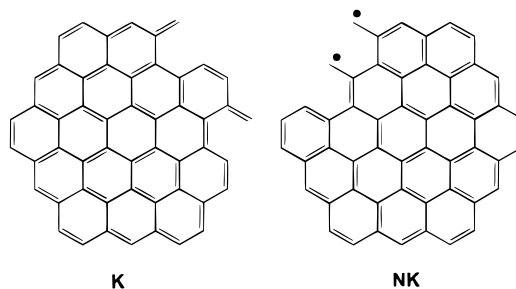
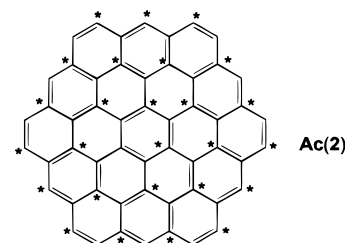
**Energy Spectra of Hydrocarbons with Defects.** The emphasis of this first communication is on the energy spectra of large hydrocarbons and 1-D ladder polymers (1-D graphite). These investigations are closely connected with the problem of the energy spectra of hydrocarbons and 1-D systems with defects, i.e., with the nature and existence of defect states in large PAHs and 1-D graphites. Of special interest are defects leading to the existence of states within the energy gap, Tamm states<sup>45,46</sup> or Shockley states<sup>47</sup> (see also ref 29). The investigation of localized defect states of PAHs and 1-D graphites is also related to the design of high-spin systems with magnetic (ferro or antiferro) ordering.<sup>48</sup>

Here, we give only a few examples that should illustrate that the problem of defect states is very complex and requires extensive and systematic investigations that are in progress.

Dependent on the type and the topology of defects (vacancies) in an even closed-shell alternant Kekule  $\pi$  system, the resulting systems are either closed-shell Kekule systems or open-shell ones. If the resulting system is a nonclassical (non-Kekule)

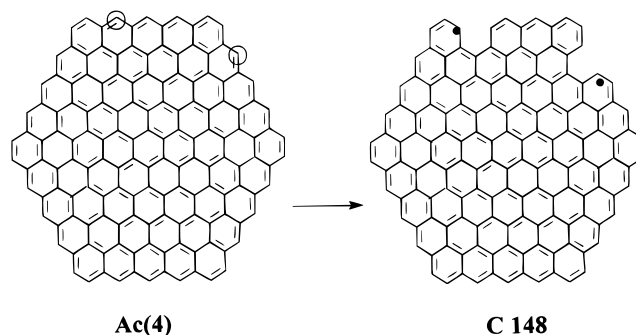
hydrocarbon that has  $\{S\}$  starred and  $\{R\}$  nonstarred  $\pi$  centers in accordance with the Coulson–Rushbrooke–Longuet–Higgins theorem,<sup>49,50</sup> then the hydrocarbon has  $S-R$  nonbonding MOs (NBMO).

The closed-shell hydrocarbon **Ac(2)** gives rise to either a closed-shell hydrocarbon **K** or a non-Kekule hydrocarbon **NK** depending on the topology of the vacancies.



Hydrocarbon **K** possesses a singlet ground state with an EG of  $\Delta E(\text{EHF}) = 1.628$  eV (result without geometry optimization), and the hydrocarbon **NK** has  $27^* - 25 = 2$  NBMOs, which are situated in the center of EG with  $\Delta E(\text{EHF}) = 2.340$  eV. The ground state of hydrocarbon **NK** is a high-spin triplet. Using the four-electron four MOs CI scheme (see ref 51) for the singlet–triplet splitting  $\Delta E_{\text{ST}} = E_{\text{S}} - E_{\text{T}}$ , one obtains for hydrocarbon **NK** a value on the order of magnitude of 0.1 eV.

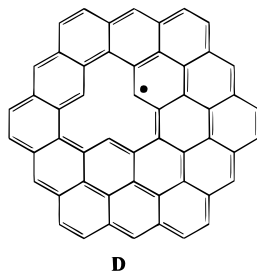
The closed-shell PAH **Ac(4)** transforms into the non-Kekule hydrocarbon **C 148**. The MO scheme of the non-Kekule



hydrocarbon **C 148** is characterized by  $75^* - 73 = 2$  NBMOs. The ground state of the hydrocarbon is also a high-spin triplet one with  $\Delta E_{\text{ST}} = E_{\text{S}} - E_{\text{T}} = \sim 0.1$  eV.

In all these cases of hydrocarbons, the vacancies are essentially surface “perturbations” that lead to the existence of NBMOs within the energy gap. This means that the NBMOs can be considered as surface or Tamm states.<sup>45,46</sup>

A doublet hydrocarbon **D** can be derived from **Ac(2)** by removing a C atom not from the periphery but from the internal part of the molecule (“point defect”). The single occupied NBMO of **D** is in the middle of the EG of  $\Delta E = 1.736$  eV.



## Conclusions

Theoretical investigations of the energy spectra of homologous polycyclic aromatic hydrocarbons with a very large number of carbon atoms ( $N \approx 10^3$ ) and of polymers having different types of edge structures suggest the following important conclusions.

(i) The  $\pi$  systems investigated in this paper are predicted to possess semiconductor properties with a nonzero energy gap when the electron correlation, the differential repulsion of the electrons, is taken into account. This result corresponds to the Hubbard–Mott model<sup>35,52</sup> of the metal dielectric transition. However, the limit value  $\Delta E(\infty)$  depends on the edge structure of the hydrocarbons and the polymers, respectively. There is a qualitative relation between the values  $\Delta E(\infty)$  of the hydrocarbons and the corresponding polymers with the same edge structure.

(ii) The main contribution to EG ( $n \gg 1$ ) is caused by electron correlation, while the topological and geometrical contributions are zero or very small.

(iii) Point defects created by removing one or more C atoms from the hydrocarbons cause levels in the energy gap.

The results raise the question of whether the energy spectra of real graphite can be described by those of very large, perturbed hydrocarbons. Investigations in this direction are in progress.

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