

Energy Spectra of One-Dimensional Stacks of Polycyclic Aromatic Hydrocarbons without Defects

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Received: June 18, 2003; In Final Form: January 22, 2004

The energy spectra of one-dimensional (1-D) stacks consisting of large π – π interacting polycyclic aromatic hydrocarbons (PAH) have been investigated theoretically with the Bloch band theory, taking into account electron correlation. It is shown that the band gap ΔE is different from zero ($\Delta E > \sim 0.8$ eV) for 1-D stacks consisting of PAHs with different topology, symmetry, and a number of π -centers $N \leq 10^2$, i.e., the ground state of the stacks is a dielectric one.

1. Introduction

One-dimensional (1-D) stacks of π -electron systems, especially polycyclic aromatic hydrocarbons (PAH), are candidates for new materials with unique electronic properties, e.g., electric conductivity, photoconductivity (see refs 1–4 and references given therein), or magnetic properties.^{5–8} Simultaneously, they are real models for nanometer-scaled graphites (nanographites).

There are two classes of 1-D stacks consisting of PAHs or their derivatives: (i) systems (stacks) without defects and with a singlet ground state and (ii) stacks consisting of PAHs with different types of defect states (Tamm, Schottky, Frenkel, or chemisorption states, respectively), with a singlet or a multiplet (high-spin) ground state.⁹ In this first paper, we consider the band structure of systems of the first type, namely different models of 1-D stacks consisting of PAHs without defects. The energy gap (EG), ΔE , is the most important characteristic of the energy spectra of a many-electron π -system with translational symmetry. On this account the calculations are focused mainly to determine the values of ΔE .

In the literature there is little information on the band structure of 1-D stacks consisting of PAHs with a large number of π -centers. The role of orbital interaction that determines the interlayer spacing in graphite and the band structures is investigated in the paper by Yoshizawa et al.¹⁰ A qualitative discussion of the band structure of 1-D stacks is carried out in the cited paper of Bushby et al.³ in which it is said: “the UV absorption spectra of 1-D stacks show that the banding effects in the condensed state of such materials give rise to a shift in the main absorption peaks which is no more than about ~ 0.2 to 0.3 eV”.³

The experimental investigations of 1-D stacked systems formed by PAHs as elementary units with a defined macroscopic architecture, namely solid columnar discotic and liquid crystalline (LC) phases (see refs 2–4 and references given therein), have prompted the present investigations.

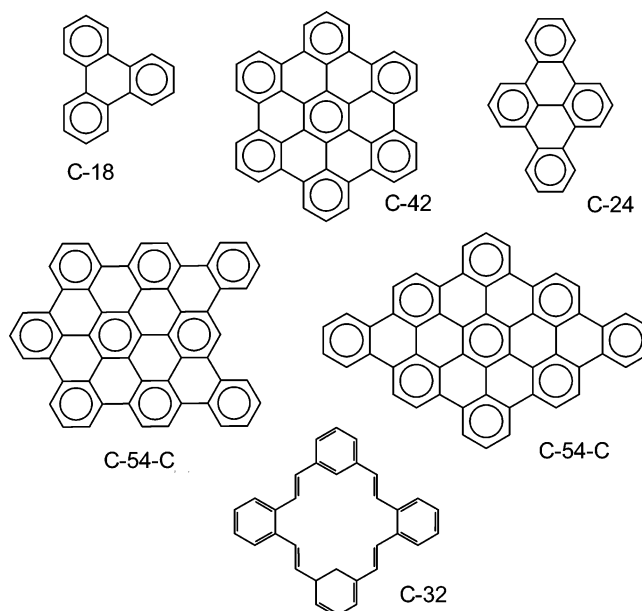


Figure 1. Investigated PAHs which build up the 1-D stacks.

2. Objects of Investigations and Models of the 1-D Stacks

The PAHs used as building units of the 1-D stacks are shown in Figure 1. All PAHs considered are Clar sextet hydrocarbons.^{11,12} An exception is the tetrabenzo-condensed [18]-annulene (C-32), which has been studied in a recent paper by Meier.⁴ Most intensively investigated have been molecular aggregates of hexabenzocoronene (HBC, C-42) and other “graphitic molecules”.^{2,13,14} The 1-D stacks of triphenylene (C-18) have been investigated in the paper by Bushby et al.³

We consider five types of 1-D stacks consisting of PAHs, shown in Figure 2: **A**, full face-to-face type where the PAHs are divided by a mirror plane of symmetry σ_h perpendicular to the translation axis; **B** and **C**, distorted systems that are characterized by a doubling of the elementary unit (EU); **D**, slipped face-to-face type with different slip angles α ; and **E**, rotated face-to-face type that are characterized by a screw axis n_m .

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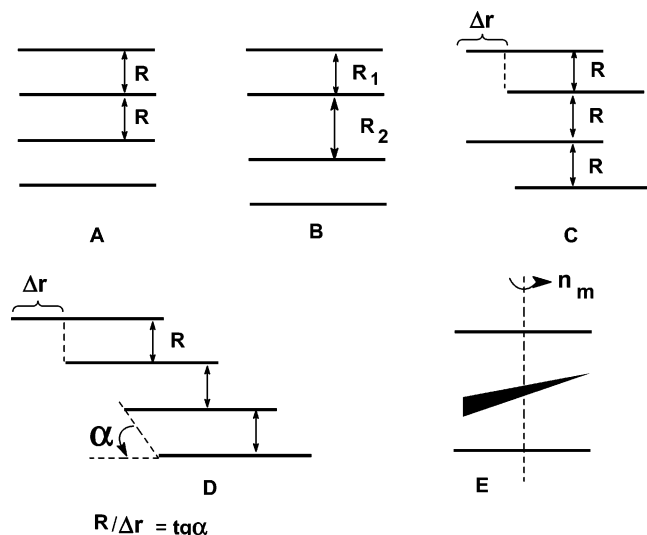


Figure 2. Different types of PAH 1-D stacks.

In a recent paper¹⁵ it was shown that the ground state of the 1-D stacked polymers consisting of PAHs with full face-to-face structure is nonbonding. This means that such structures are unstable with respect to such a distortion, which leads to a change from a full face-to-face structure to a structure with lower symmetry. The energy spectra of systems with full face-to-face arrangement of the PAHs were also investigated (see Section 4) for a comparison with the other types of stacks.

The interplanar distances R between the PAHs in dimers or 1-D stacks vary between 3.35 Å for graphite,¹⁶ 3.5 Å for HBC dimers,^{17–19} and 3.58 Å for 1-D stacks of **C-32** hydrocarbon⁴ (see also ref 20).

The stacks are considered to be 1-D systems for which the Born–Karman cyclic conditions are fulfilled.

3. Methods of Investigations

3.1. Energy Spectra of the 1-D Stacks. If we consider a 1-D system with $N = 2n$ π -centers in the EU and one electron per π -center, the Bloch functions can be represented as follows:

$$|k_{f(e)}\rangle = N^{-1/2} \sum_{f(e)} \sum_{\mu} \sum_r C_{rf(e)}(k) \exp(-ik\mu) |r, \mu\rangle \quad (1)$$

($k \in [-\pi, \pi]$) is the wave vector, μ denotes the number of the EU, and $|r, \mu\rangle$ is the r th AO within the μ th EU; $f(e)$ is the band index for the filled (empty) bands. In the Hückel–Hubbard version²¹ of the Bloch method the MO energies $\epsilon(k)$ are eigenvalues of the energy matrix:²²

$$\mathbf{E}(k) = \mathbf{E}_0 + \mathbf{V} \exp(ik) + \mathbf{V}^+ \exp(-ik) \quad (2)$$

where \mathbf{E}_0 is the energy matrix for the EU, \mathbf{V} is the interaction matrix between neighboring EUs (μ th and $(\mu+1)$ th), and \mathbf{V}^+ is the transposed matrix.

3.2. Band Gap Equation. Using the alternant MO (AMO) variant of the extended Hartree–Fock (EHF) method²³ it was shown^{24,25} that the EG of an arbitrary π -conjugated system with a singlet ground state is given by the expression:

$$\Delta E^\sigma(\text{AMO}) = \{[\Delta E(\text{HF}) + \Delta_1(\sigma)_{\text{corr}}]^2 + \Delta^2(\sigma)_{\text{corr}}\}^{1/2} = \{[\Delta_{\text{top}} + \Delta_{\text{geom}} + \Delta_1(\sigma)_{\text{corr}}]^2 + \Delta^2(\sigma)_{\text{corr}}\}^{1/2} \quad (3)$$

In eq 3, $\Delta E(\text{HF}) = \Delta_{\text{top}} + \Delta_{\text{geom}}$ is the width of the EG calculated in the one-electron Hückel–Hubbard²¹ approximation

(eq 2). Δ_{top} expresses the width of the EG in the topological approximation, calculated with equal values of the bond distances and therefore with equal resonance integrals β between neighboring π -centers in the PAH; $\Delta_{\text{top}} + \Delta_{\text{geom}}$ is the width of the EG taking into account changes of the bond distances corresponding to the real geometry of the PAHs forming the 1-D system.

In the general case the correlation corrections $\Delta_1(\sigma)_{\text{corr}}$ and $\Delta(\sigma)_{\text{corr}}$ differ for MOs with different spin ($\sigma \in \alpha, \beta$). There is a significant difference in the formalisms to calculate the correlation correction contribution to the EG of homonuclear alternant π -electron systems (AS) and of nonalternant and heteronuclear π -electron systems, respectively.

The correlation corrections $\Delta_1(\sigma)_{\text{corr}}$ and $\Delta(\sigma)_{\text{corr}}$ are determined (depend on) by the nonuniform charge distribution in the π -system. The correlation correction $\Delta_1(\sigma)_{\text{corr}}$ is equal to the following expression, which is formulated in more detail in ref 25 (see eq 1):

$$\begin{aligned} \Delta_1(\sigma)_{\text{corr}} &= \sum_r Q_r(k) A_r(\sigma) = \\ &\sum_r [C_{re}(k) C_{re}^*(k) - C_{rf}(k) C_{rf}^*(k)] A_r(\sigma) \\ \Delta_1(\sigma)_{\text{corr}} &= \sum_r P_r(k) A_r(\sigma) = \\ &\sum_r [C_{re}(k) C_{re}^*(k) + C_{rf}(k) C_{rf}^*(k)] A_r(\sigma) \end{aligned}$$

In the case of homonuclear alternant systems from the Coulson–Rushbrooke–Longuet–Higgins (pair) theorem it follows²⁶ that $Q_r(k) = 0$ and $\Delta_1(\sigma)_{\text{corr}} = 0$, and eq 4 obtains the form identical for the AMOs with α and β spin:

$$\Delta E^\alpha(\text{AMO}) = \Delta E^\beta(\text{AMO}) = \Delta E = \sqrt{(\Delta_{\text{top}} + \Delta_{\text{geom}})^2 + \Delta_{\text{corr}}^2} \quad (4)$$

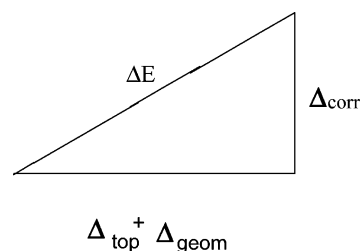
In this case the correlation correction is given by:

$$\Delta_{\text{corr}} = 2\delta\gamma$$

where γ is the one-center Coulomb repulsion integral of the carbon π -centers (Hubbard parameter).²¹

Equation 4 has a clear geometrical meaning: the three quantities ΔE , $\Delta E(\text{HF})$, and Δ_{corr} are connected by means of the *Pythagoras* relation (see Scheme 1):

SCHEME 1



The dimensionless parameter δ fulfills eq 5:

$$N\delta = \delta \sum_f \sum_k \gamma / [\delta^2 \gamma^2 + \beta^2 e_f^2(k)]^{1/2} \quad (5)$$

$N = 2n$ is the number of π -centers, and $\epsilon(k)$ are the MO energies. Equation 5 always has a trivial solution $\delta = 0$, i.e.,

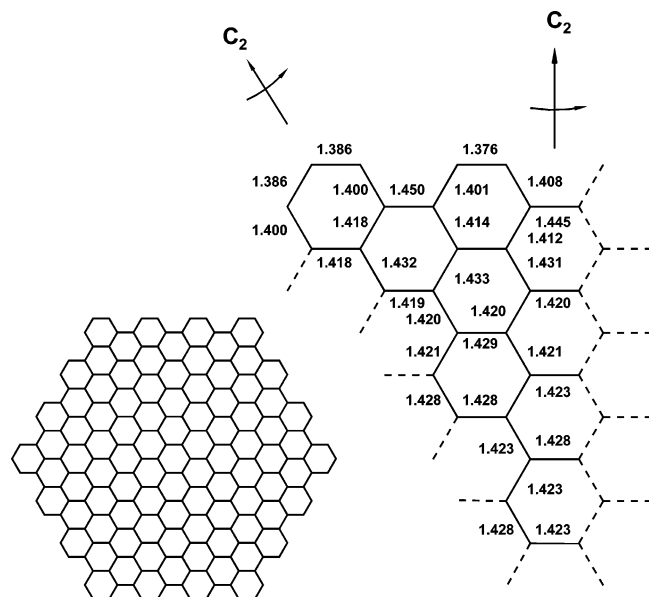


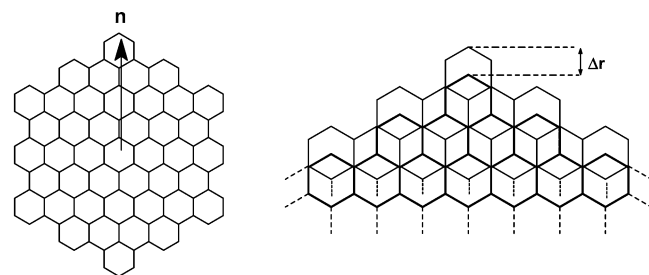
Figure 5. Bond lengths of a PAH (in Å) with 222 π -centers calculated by means of the extended SSH method. Because the molecule belongs to the D_{6h} symmetry group, only one part is given.

TABLE 1: Calculated Values of the Components of the EG (See Eq 4) of PAHs $\text{Ph}(n)$, $\Delta E(m)$, with Different Values of the Number N of π -Centers, and of Corresponding Dimers $\Delta E(d)$, Respectively^a

n	N	Δ_{top}	Δ_{geom}	Δ_{corr}	$\Delta E(m)$	$\Delta E(d)$
1	42	2.231	0.106	0	2.237	1.992
2	114	1.397	0.065	0	1.462	1.205
3	222	1.014	0.042	0	1.055	0.865
4	366	0.795	0.030	0	0.825	0.674
5	546	0.654	0.021	0	0.675	0.555
6	762	0.555	0.014	0.035	0.570	0.475
7	1014	0.482	0.009	0.114	0.504	0.418
9	1626	0.381	0.002	0.210	0.437	0.345
10	1986	0.345	~0	0.201	0.399	0.306
∞	∞	0.196 ^b	0	0.183 ^b	0.293 ^c	0.260 ^c
∞	∞	0.196 ^b	0	0.183 ^b	0.268 ^d	

^a The results of dimers are calculated for an interplanar distance $R = 3.35$ Å. All entries are in eV. ^b Values calculated by means of Aitken's formula: three-point Pade approximation,³⁶ last three values of Δ_{top} and Δ_{corr} . ^c Calculated with the last three values of ΔE . ^d Calculated with $\Delta_{\text{top}}(\infty)$ and $\Delta_{\text{corr}}(\infty)$ by means of eq 4.

SCHEME 2



$\text{Ph}(n)$, $n = 0$ (benzene), 1, 2,...

Dimers

$$N = 6(1 + 3n + 3n^2)$$

decreases and monotonically approaches zero. This is illustrated in Table 1 in which are collected the results of the band gap components of the hydrocarbons $\text{Ph}(n)$ (Scheme 2). The geometrical component has large values for PAHs with small numbers of π -centers and clear alternation in bond lengths as for the hydrocarbons **C-18** and **C-32** (see Tables 2–6).

TABLE 2: Calculated Values of the Components of the EG in the 1-D Stacks Composed of C-18 PAH (Models B and C, Scheme 4)^a

model	R_1	R_2	Δ_{top}^b	Δ_{geom}^c	Δ_{corr}	ΔE
A	3.35	3.35	2.132	0.096	0	2.228
B	3.35	3.50	2.318	0.110	0	2.428
B	3.35	3.80	2.400	0.106	0	2.506
C	3.35	3.35	2.592	0.101	0	2.692

^a All entries are in eV. ^b Calculated for ideal geometry of **C-18** (equal values of the bond distances). ^c Calculated with optimized geometry by means of the extended SSH method.

TABLE 3: Calculated Values of the Components of the EG of 1-D Stacks with Different Values of the Slip Parameter Δr (Å)^a

model	Δr	Δ_{top}	Δ_{geom}	Δ_{corr}	ΔE
D	2.424	2.770	0.109	0	2.872
D	4.848	3.002	0.118	0	3.120
D	> 7.0	3.283 ^b	0.132 ^b	0	3.415 ^b
E	$\Theta = 60^\circ$	3.080	0.108	0	3.188

^a The interplanar distance is $R = 3.5$ Å. All energy entries are in eV. ^b Values of the isolated molecule.

TABLE 4: Calculated Values of the Components of the EG in 1-D Stacks of C-24 (Model D) with Different Values of the Slip Parameter Δr (Å)^a

Δr	Δ_{top}	Δ_{geom}	Δ_{corr}	ΔE
0	1.512	0.158	0	1.670
2.424	2.038	0.144	0	2.182
4.848	2.608	0.138	0	2.746
> 5.0	2.664 ^b	0.130 ^b	0	2.794 ^b

^a The interplanar distance is $R = 3.35$ Å. All energies entries are in eV. ^b Values of the isolate (noninteracting) molecule.

TABLE 5: Calculated Values of the Components to the EG of 1-D Stacks of C-24 with Different Values of the Interplanar Distances R_1 and R_2 ^a

R_1	R_2	Δ_{top}	ΔE
3.35	3.35	1.968	1.968
3.35	3.60	2.073	2.073
3.35	3.80	2.131	2.131
3.35	> 4.00	2.256 ^b	2.256 ^b

^a The slip parameter is $\Delta r = 2.424$ Å. The results are obtained with ideal geometry of the PAHs. $\Delta_{\text{geom}} = 0$, and $\Delta_{\text{corr}} = 0$. All entries are in eV. ^b Values for isolated (noninteracting) dimers. **C-24**, Model **B**, distorted system with doubling of the EUs (Scheme 7).

TABLE 6: Calculated Values of the Components of the EG in 1-D Stacks of C-32 (Model D) with Different Values of the Slip Parameter Δr (Å)^a

Δr	Δ_{top}	Δ_{geom}	Δ_{corr}	ΔE
0.0	1.049	0.403	1.206	1.887
1.4	1.480	0.364	1.347	2.283
2.8	1.712	0.404	1.201	2.433
> 10.5	~1.780	~0.314	~1.223	2.425 ^b

^a The interplanar distance is $R = 3.58$ Å.⁴ All energy entries are in eV. ^b Values of the isolated molecule.

In refs 27 and 32–34 it has been shown that the energy gap ΔE for PAHs with a large number N of carbon atoms and different edge structure and symmetry is different from zero if the electron correlation contribution is taken into account. Also in the asymptotic case $N \rightarrow \infty$ (2-D model of graphite) $\Delta E \neq 0$. This conclusion is also valid for dimers built up of corresponding PAHs. This is illustrated in Table 1 in which the results of the hydrocarbons $\text{Ph}(n)$ (Scheme 2) are compared and the results of the corresponding dimers are given.

TABLE 7: Calculated Values of the Components of the EG in 1-D Stacks of C-42 (Model D, Scheme 10) with Different Values of the Slip Parameter Δr (Å)^a

Δr	Δ_{top}	Δ_{corr}	ΔE
0 ^b	1.120	0.209	1.147
1.4	1.667	0	1.667
5.6	1.752	0	1.752
9.8	1.997	0	1.997
>10.5	~2.223 ^c	0	2.223

^a The interplanar distance is $R = 3.35$ Å. The calculations were carried out by taking into account the interaction only between the first neighbor π -centers. $\beta(2p\sigma-2p\sigma) = -2.4$ eV, $S(3.35\text{Å})/S(1.40\text{Å}) = -0.288$ eV. All energy entries are in eV. ^b Full face-to-face arrangement. ^c Values of the isolated molecule.

TABLE 8: Calculated Values of the Components of the EG in 1-D Stacks of C-42 (Model D, Scheme 10), with Different Values of Slip Parameter Δr (Å)^a

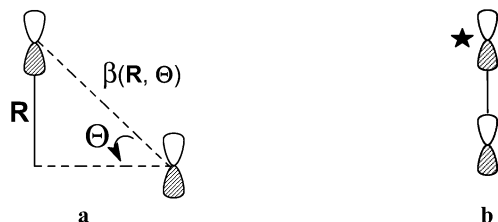
Δr	Δ_{top}	Δ_{corr}	$\Delta_{1,\text{corr}}$	ΔE
0	1.120	0.226	0.061	1.202
1.212	1.567	0.090	0.042	1.612
3.636 ^c	1.706	0.034	0.014	1.720
6.060	1.802	0	0.006	1.808
8.484	1.866	~0	~0	1.866
>10	2.223	0	0	2.223 ^b

^a The interplanar distance is $R = 3.35$ Å. The results are for solutions with identical α - and β -spin AMOs: $\Delta_1(\alpha)_{\text{corr}} = \Delta_1(\beta)_{\text{corr}} = \Delta_{1,\text{corr}}$ (see eq 8). All entries are in eV. ^b Values for the isolated (noninteracting) molecule. ^c This arrangement of the HBC molecules in the 1-D stacks corresponds to the X-ray crystal structure of HBC.¹⁴

4.2. Energy Spectra of 1-D Stacks. In the general case the resonance integrals between two $2p\pi-2p\pi$ AOs and also $2p\sigma-2p\sigma$ AOs (intermolecular interaction) have been calculated with Mulliken's formula:³⁵

$$\beta(R, \Theta) = \beta_0 [S(R, \Theta)]/S(R_0) \cos \Theta$$

taking into account the angular dependence of the overlap integrals S (calculated with the value of the Slater orbital exponent: $z_C = 3.25$) (Scheme 3a). A standard value β_0 ($R_0 = 1.40$ Å) $= -2.4$ eV has been used for the resonance integral between the $2p\pi-2p\pi$ AOs of carbon atoms,^{27,32-34} and with a value $\gamma = 5.4$ eV for the one-center Coulomb integral (Hubbard parameter).²¹

SCHEME 3

In the structures where the π -centers of neighboring layers are situated one upon the other (the slip angle is $\theta = 90^\circ$) and if the interaction is taken into account only between first neighbors, the stacks are alternant systems, Scheme 3b. In this case the correlation component $\Delta_1(\sigma)_{\text{corr}} = 0$ (see eq 3) and the energy gap, ΔE , was calculated by means of eq 4.

When the second and more distant neighbors are taken into account ($\theta \neq 90^\circ$) the system is nonalternant. In this case the correlation component is $\Delta_1(\sigma)_{\text{corr}} \neq 0$, and the energy gap, ΔE , can be calculated with eq 3 (see eqs 8 and 8a). In Tables 2–9 are given the calculated values of the components to the EG in 1-D stacks composed of different PAHs and different models.

TABLE 9: Calculated Values of the Components of the EG in 1-D Stacks of C-42 (Model D) with Different Values of Slip Parameter Δr (Å)^a

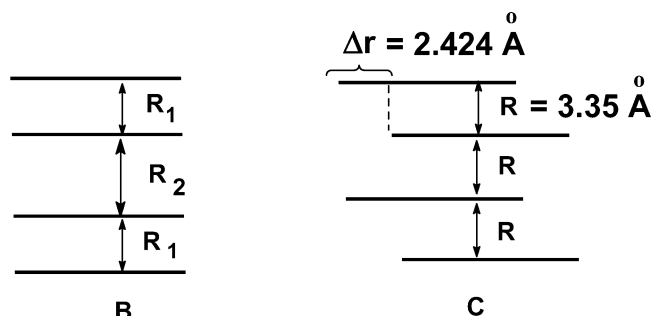
Δr	Δ_{top}	Δ_{corr}	$\Delta_1(\alpha)_{\text{corr}}$	$\Delta_1(\beta)_{\text{corr}}$	$\Delta E(\alpha)$	$\Delta E(\beta)$
0	1.120	0.186	0.068	0.062	1.202	1.197
1.212	1.567	0.134	0.047	0.044	1.620	1.617
3.636	1.706	0.035	0.031	0.029	1.737	1.736
6.060	1.802	~0	0.018	0.017	1.820	1.819
8.484	1.866	0	~0	~0		1.866

^a The interplanar distance is $R = 3.35$ Å (see Table 8). The results are for solutions with different α - and β -spin AMOs, $\Delta_1(\alpha)_{\text{corr}} \neq \Delta_1(\beta)_{\text{corr}}$ (see eq 8a). All entries are in eV.

In the following sections the energy spectra of 1-D stacks of the PAHs shown in Figure 1 are discussed. The most important feature of the band structure of the stacks with regard to the electrical properties is the energy gap. Therefore, the main point of the discussion concerns the relation between the width of the EG and the arrangements of the single molecules in the stacks in different models presented in Section 2 and shown in Figure 2.

1-D Stacks Consisting of C-18: (a) Models A, B, and C. In accordance with the considerations in Section 2 the interaction between PAHs in an arrangement corresponding to model A (full face-to-face) is nonbonding, i.e., the stacking does not lead to a stabilization of the 1-D system. Some possible types of symmetry breaking in a stack composed of PAHs correspond to the models B, C, D, and E, shown in Figure 2.

In Table 2 are given the calculated values of the components to the EG in 1-D stacks composed of C-18 PAHs with an arrangement of triphenylene molecules corresponding to models A ($R_1 = R_2$), B, and C (see Scheme 4). The calculations were carried out taking into account the interaction between first ($2p\sigma-2p\sigma$) neighboring π -centers. Models B and C are characterized by a doubling of the EU.

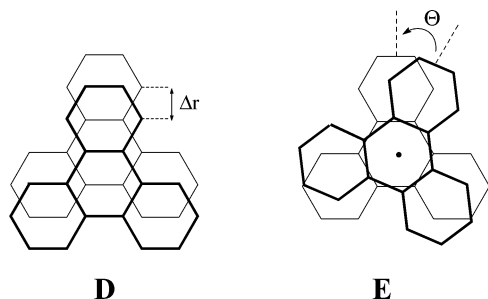
SCHEME 4

It can be seen from the values in Table 2 that the width of the EG is not influenced significantly by the arrangement of triphenylene molecules in the stacks. The main contribution to the EG is the topological component while the geometrical component is very small, and the correlation correction is zero in each case.

(b) Models D and E. In Table 3 are given the calculated values of the components to the EG of 1-D stacks composed of PAHs C-18, models D and E (Scheme 5). The calculations were carried out taking into account the interaction between first neighboring π -centers.

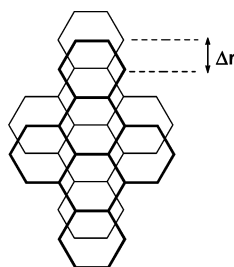
For the distorted structures B and C, as well as for the structures of types D and E, the energy gap has significant values for all used values of the parameters R , Δr , and θ which determine the deviation from the full face-to-face structure. The larger the deviation from the full face-to-face structure (larger values of R , Δr , or θ), the larger the EG (ΔE values).

SCHEME 5

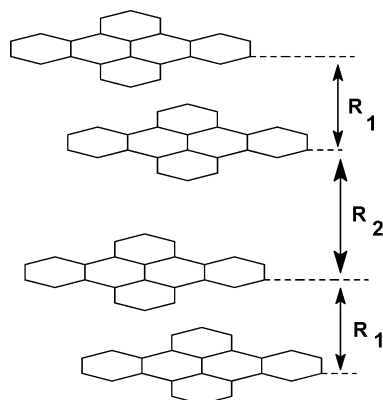


1-D Stacks Consisting of C-24 (Model D, Scheme 6). The calculated values of the components to the EG of stack models **D** (Scheme 6) and **B** (Scheme 7) of PAH **C-24** are given in

SCHEME 6



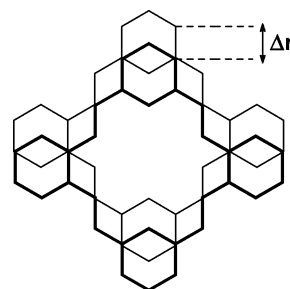
SCHEME 7



Tables 4 and 5. From Table 4 it can be seen that the EG of the stack decreases with decreasing slip parameter Δr . To create stacks with a small band gap the stacking of the single molecules should be near a full face-to-face arrangement. As with the former examples, the geometrical component to the EG is small and the correlation correction zero in stack model **D**. In model **B** is realized a distorted system with doubling of the EU caused by different intermolecular distances between the single molecules (Figure 2). In this case both the geometrical and the correlation contributions to the EG are zero, and the width of the EG is determined only by the topology of the stack. In relation to noninteracting dimers, the width of the EG in the stack is reduced.

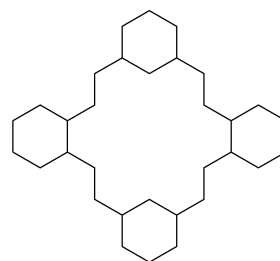
1-D Stacks Consisting of C-32 (Model D, Scheme 8). The isolated **C-32** molecule and the corresponding 1-D stacks are the only systems for which the correlation contribution to the EG has a very large value (see Table 6). This is not an unexpected result. PAH **C-32** is a [18]annulene π -system condensed with benzene rings. The **C-30** hydrocarbon is the perimeter model³⁷ of PAH **C-32** with essential features of a cyclopolyene system for which it is known that the correlation

SCHEME 8



correction has a large value.^{38,39} In Scheme 9 are compared the calculated values of the topological and the correlation components of the energy gap of the isolated **C-32** molecule and the theoretical model of an annulene with 30 π -centers. The results are obtained with optimized geometries of the molecules.

SCHEME 9

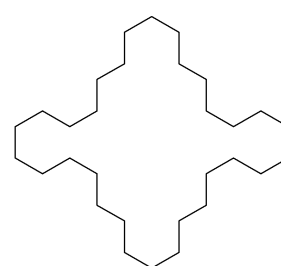
**C - 32**

$$\Delta_{\text{top}} = 1.780 \text{ eV}$$

$$\Delta_{\text{geom}} = 0.314 \text{ eV}$$

$$\Delta_{\text{corr}} = 1.223 \text{ eV}$$

$$\Delta E = 2.425 \text{ eV}$$

**C - 30**

$$\Delta_{\text{top}} = 1.003 \text{ eV}$$

$$\Delta_{\text{geom}} = 1.07 \text{ eV}$$

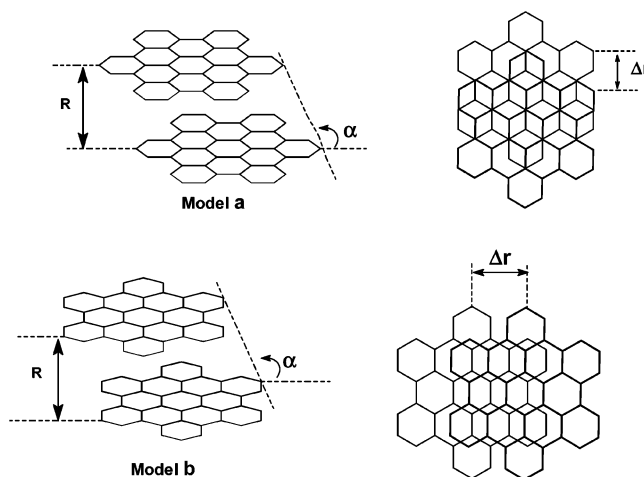
$$\Delta_{\text{corr}} = 2.107 \text{ eV}$$

$$\Delta E = 2.319 \text{ eV}$$

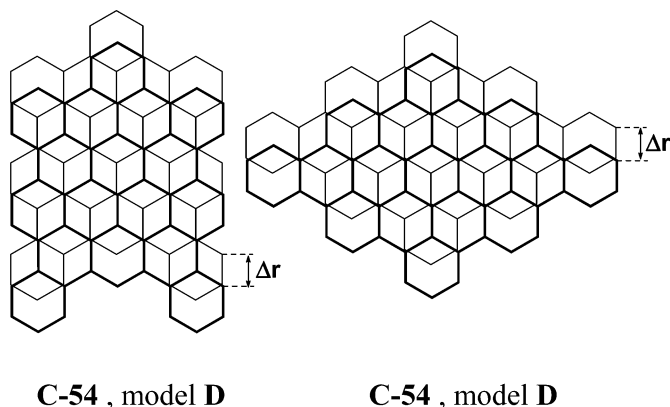
Stacking of **C-32** molecules corresponding to model **D** results in a decrease of the EG width (see Table 6). With increasing slip parameter, Δr , the geometrical contribution, Δ_{geom} , and the correlation correction, Δ_{corr} , are nearly constant, but the topological term, Δ_{top} , is increased.

1-D Stacks Consisting of C-42 (HBC). Two types of stacks of HBC shown in Scheme 10 have been investigated. In the case of 1-D stacks consisting of large PAHs ($N > 40$ π -centers)

SCHEME 10



SCHEME 11



The molecules belong to

C_{2v} symmetry group

D_{2h} symmetry group

TABLE 10: Calculated Values of the Components of the EG of 1-D Stacks of C-54 (Model D) with D_{2h} and C_{2v} Symmetry (Scheme 11) with Different Values of the Slip Parameter Δr (Å)^a

symmetry	Δr	1-D stack			dimer		
		Δ_{top}	Δ_{corr}	ΔE	Δ_{top}	Δ_{corr}	ΔE
C_{2v}	0	747	0.910	1.177	1.317	0.601	1.447
D_{2h}	0	0.689	0.895	1.129	1.256	0.623	1.402
C_{2v}	1.4 ^b	1.572	0	1.572	1.718	0	1.718
D_{2h}	1.4 ^b	1.370	0	1.370	1.603	0	1.603
C_{2v}	2.8 ^d	1.370	0	1.370	1.645	0	1.744
D_{2h}	2.8 ^d	1.670	0	1.670	1.744	0	1.645
C_{2v}	5.6 ^b	1.754	0	1.754	1.829	0	1.829
D_{2h}	5.6 ^b	1.426	0	1.426	1.636	0	1.636
C_{2v}	7.0 ^d	1.510	0	1.510	1.701	0	1.701
D_{2h}	7.0 ^d	1.804	0	1.804	1.818	0	1.818
C_{2v}	9.8 ^b	1.880	0	1.880	1.886	0	1.886
D_{2h}	9.8 ^b	1.690	0	1.690	1.834	0	1.834
C_{2v}	11.2 ^d	1.776	0	1.776	1.834	0	1.834
D_{2h}	11.2 ^d	1.834	0	1.834	1.891	0	1.891
C_{2v}	>11.2	1.893	0	1.893	1.893 ^c	0	1.893 ^c
D_{2h}	>11.2	1.834	0	1.834	1.834 ^c	0	1.834 ^c

^a The interplanar distance is $R = 3.35$ Å. In the table are also given the results of the corresponding dimers. All entries are in eV. ^b $\Delta r = (2 + 6n) \times 0.7$ Å ($n = 0, 1, 2, \dots$) first group; $\Delta r = (4 + 6n) \times 0.7$ Å ($n = 0, 1, 2, \dots$), second group. ^c Values for isolated molecules. ^d Depending on the value of the slip parameter Δr , the structures of the stacks and of the dimers belong to two different groups. For the first group ($\Delta r = (2 + 6n) \times 0.7$ Å), $\Delta E(C_{2v}) < \Delta E(D_{2h})$. The opposite is true for the second group ($\Delta r = (4 + 6n) \times 0.7$ Å): $\Delta E(C_{2v}) > \Delta E(D_{2h})$.

the geometry component of the EG is $\Delta_{\text{geom}} < 0.08$ eV. For this reason the results given in Tables 7–9 are obtained with ideal geometry of the PAHs. For both models **a** and **b** shown in Scheme 10, nearly the same values of ΔE have been obtained for comparable values of the slip parameter Δr . Therefore, in Tables 7–9 only the results of model **a** (Scheme 10) are given.

As can be seen in Table 9, the values of the correlation corrections which depend on the nonequal distribution of the electron density, $\Delta_{1,\text{corr}}(\sigma)$ ($\sigma \in \alpha, \beta$), are also positive and are close in value to the corrections $\Delta_{1,\text{corr}}(\alpha) = \Delta_{1,\text{corr}}(\beta) = \Delta_{1,\text{corr}}$. In all cases the correlation corrections $\Delta_{1,\text{corr}}$ and $\Delta_{1(\sigma)\text{corr}}$ are small in value and their influence on the value of ΔE is insignificant. The smaller the slip parameter, Δr , in the stacking modes **C** and **D** (Figure 2) (and models **a** and **b**, Scheme 10) the smaller the EG width.

1-D Stacks Consisting of C-54. To investigate the influence of the symmetry of PAHs which build up 1-D systems, in Table 10 are compared the results for the iso- π -electronic PAHs **C-54** arranged in model **D** but with different symmetry: C_{2v} and D_{2h} (Scheme 11). For all values of the parameter Δr , the values of ΔE are very close. With increase of Δr the values of ΔE increase monotonically (in both groups) and tend to the value of the isolated molecules. With the exception of the full face-to-face arrangement of both iso- π -electronic **C-54** molecules in stacking model **D** with C_{2v} and D_{2d} symmetry and also in dimers the geometrical component and the correlation correction are zero.

The estimates of the one-particle excitation energies, ΔE , in this work are direct (vertical) electron transitions, for which the absorption of the photon is not connected with absorption or release of a phonon. The energy of the lattice distortions of a hydrocarbon with a large number of π -centers is of the order of magnitude $\hbar\omega_q \sim 0.2\text{--}0.3$ eV.⁴⁰ Denoting the energy of a phonon in PAH with $\hbar\omega_q$, the energy of the indirect transition, $\Delta\epsilon_q$, i.e., the transition where along with the absorption of a photon, a phonon is absorbed or released, will be as follows:⁴⁰

$$\Delta\epsilon_q = \Delta E \pm \hbar\omega_q$$

This means that if the width of the EG is low ($\Delta E < 0.3$ eV), the ΔE value becomes comparable with that of phonons:

$$\Delta E \sim \hbar\omega_q$$

5. Conclusions

The numerical results of the energy gap of 1-D stacked polymers composed of π - π interacting large polycyclic aromatic hydrocarbons as well as of a [18]annulene condensed with benzene rings with different symmetry and with different arrangement of the molecules within the stacks lead to the following general conclusions:

(i) For all arrangements of the molecules within the 1-D stacks (the structures are shown in Figures 1 and 2) the value of the energy gap is different from zero, $\Delta E \neq 0$. This means that the ground state of these systems is a dielectric one.

(ii) This conclusion is valid also for Peierls systems for which the 1-D stacks are characterized by **doubling** of the elementary units.

(iii) In all cases $\Delta E > 0.8$ eV. Exceptions are only systems with full face-to-face arrangement; however, they are symmetrically forbidden (nonbonding).

(iv) The above results are valid for 1-D stacks for which the Born–Karman cyclic conditions are fulfilled.

(v) The energy gap of dimers composed of PAHs with different numbers of π -centers in the asymptotic case ($N \rightarrow \infty$) is also different from zero.

Investigations already in progress show that the energy spectra and the physical properties, e.g., electrical and magnetic properties, are strongly changed for 1-D stacks composed of PAHs with different types of defects: Tamm, Shottky, Frenkel, and Shokley defects. The results of these investigations will be published soon in the second part of this series.

Acknowledgment. This work was supported by the Sächsische Staatsministerium für Wissenschaft und Kunst, the Naturwissenschaftliches Theoretisches Zentrum, Universität Leipzig (N.T.), and the Deutsche Forschungsgemeinschaft (N.T., A.S.).

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