

ARTICLES

Bandgap Oscillation in Polyphenanthrenes

Kazunari Yoshizawa,^{*,†} Kazuyuki Yahara,^{†,‡} Kazuyoshi Tanaka,[†] and Tokio Yamabe^{*,†,‡}*Department of Molecular Engineering, Kyoto University, Sakyo-ku, Kyoto 606-01, Japan, and Institute for Fundamental Chemistry, 34-4 Takano-Nishihiraki-cho, Sakyo-ku, Kyoto 606, Japan**Received: August 27, 1997; In Final Form: November 13, 1997[⊗]*

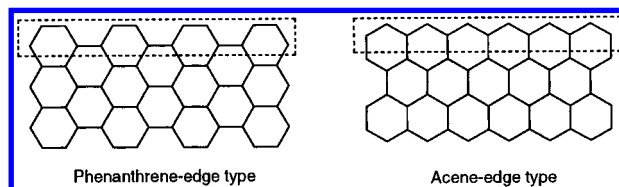
The electronic structures of carbon-based ladder polymers and polynuclear aromatic hydrocarbons (PAHs) with acene- and phenanthrene-edge structures are studied with an approximate molecular-orbital method. The difference between polyacene and polyphenanthrene can be derived from detailed orbital interaction analyses of anthracene and phenanthrene. The fragment molecular-orbital (FMO) method successfully characterizes the distinct electronic structures of the two small PAHs with different types of edges. We shed light on the electronic structures of ladder polymers with the phenanthrene-edge structure, PPh(n), in which n is the number of *cis*-polyene chains included. With an increase in width of the ladder polymers, the bandgap of PPh(n) approaches zero with a behavior that has a periodicity of 3. The PPh(n) series are classified into three subgroups: small-gap (metallic) PPh($3m + 1$), large-gap PPh($3m + 2$), and medium-gap PPh($3m$), where $m = 0, 1, 2, \dots$. The oscillating behavior in the bandgap of the three subgroups is analyzed from the viewpoint of interchain interactions in the frontier crystal orbitals.

Introduction

Much interest is now directed to the electronic properties of graphite and highly condensed polynuclear aromatic hydrocarbons (PAHs) because of their great technological importance as an electrode material for lithium-ion rechargeable batteries. Control of the electronic structures as well as the nanosized structures of such carbon-based materials is essential for the development of lithium-ion batteries of high quality.^{1–4} Highly condensed PAH materials that afford an extremely high capacity over 1000 mA h g^{−1} are prepared by heat treatment of various kinds of polymers such as phenol–formaldehyde resin¹ and poly-*p*-phenylene.² Extensive structural analyses have been carried out to characterize pyrolytic carbons that are supposed to consist of highly condensed PAHs, but their structure is a problem under debate. Electrochemical aspects of important conducting polymers for recent rechargeable batteries have been discussed in a review paper.⁵

Theoretical studies at various levels have clarified that the electronic properties of PAHs significantly depend on their molecular sizes and edge structures.^{6–10} There are several prototypes for the edge structures of PAHs: one of the most important edge structures is “phenanthrene-edge type” (or arm-chair-edge type) and another is “acene-edge type” (or zigzag-edge type), as shown in Scheme 1. The characteristics of the frontier orbitals, the orbitals in the vicinity of the Fermi level, significantly depend on the edge structures of PAHs.^{8,10} In the acene-edge structure, the frontier orbitals are localized at the edges, whereas in the phenanthrene-edge structure the frontier orbitals are distributed evenly over the carbon structure.

SCHEME 1



There have been a lot of theoretical investigations on the electronic structures of one-dimensional graphite polymers by Whangbo, Hoffmann, and Woodward,¹¹ Tanaka and Yamabe et al.,¹² Brédas et al.,¹³ Kertesz et al.,¹⁴ Tyutyulkov et al.,¹⁵ and Fujita et al.¹⁶ In some of these studies,^{11,12b,14a,b} polyacene is a special interest for designing a small-gap conducting polymer. Recently, experimental efforts toward the synthesis of carbon-based ladder polymers or oligomers have been made by Müllen et al.,¹⁷ Herndon et al.,¹⁸ and Mallory et al.¹⁹ The control of bandgap in π -conjugated systems including ladder polymers has been recently reviewed.²⁰

The electronic properties of small PAHs have been extensively studied at various levels of theory^{21–25} in order to clarify the correlation between structure and stability in PAHs. Clar's concept on “aromatic sextet”²¹ enables us to qualitatively predict the reactivity of PAHs. Since fully benzenoid molecules are supposed to be of low reactivity, a structure that includes more aromatic sextets is energetically more stable. Dewar's resonance energy (DRE)²² is often used as an index to predict the stability of PAHs, and there is a chemically significant correlation between the DRE and edge structure of PAHs.⁶

To pursue the relation between Clar's concept and resonance theory, topological analyses have been carried out. Hosoya et al.²³ analytically investigated the relation between aromaticity and stability for PAHs. Moreover, Randic et al.²⁴ applied a

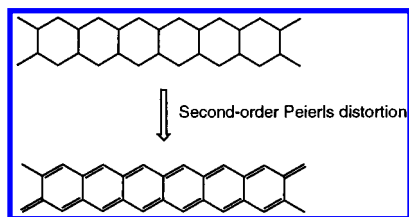
* Corresponding author.

† Kyoto University.

‡ Institute for Fundamental Chemistry.

⊗ Abstract published in *Advance ACS Abstracts*, December 15, 1997.

SCHEME 2



graph theoretical analysis to characterize aromaticity and antiaromaticity. Aihara et al.²⁵ proposed topological resonance energy (TRE) and percentage resonance energy (%RE) as indexes of aromatic stability.

In this paper, we discuss in terms of orbital interactions the correlation between the electronic properties and edge structures of carbon-based ladder polymers as well as PAHs. We will consider the reason why the electronic properties of ladder polymers depend on their edge structures. A main purpose of this paper is to give a better understanding of the electronic properties of such one-dimensional polymers, especially phenanthrene-edge type rather than acene-edge type. For this purpose, we use the fragment molecular orbital (FMO) method²⁶ based on the extended Hückel approximation.²⁷

Models and Computational Details

Band-structure calculations and FMO analyses based on the extended Hückel method were carried out with YAEHMOP.²⁸ This approximate method models general orbital-energy trends, bandgaps, orbital interactions, and major charge shifts well. Parameters used for carbon and hydrogen atoms are C 2s ($H_{ii} = -21.4$ eV, $\zeta = 1.625$), C 2p ($H_{ii} = -11.4$ eV, $\zeta = 1.625$), and H 1s ($H_{ii} = -13.6$ eV, $\zeta = 1.3$), in which H_{ii} and ζ are the orbital energies and Slater exponents, respectively. A 50K point set was used for the band structure and density of states (DOS) calculations. Lattice sums were taken to the fifth-nearest neighbors in band-structure calculations.

In this study, all C–C and C–H bond distances were set to be 1.4 and 1.09 Å, respectively. The “first-order” Peierls distortion²⁹ that occurs, e.g., in a single polyene chain, significantly affects the structure and electronic properties of one-dimensional systems. However, the effect of C–C bond-length alternation in carbon-based ladder polymers is likely to be small because it is a consequence of interchain interactions, a “second-order” perturbation effect.^{14a,30,31} For example, the undistorted structure of polyacene, which can be viewed as two interacting polyene chains, is energetically unfavorable, and it will be transformed into a bond-length alternant form in which there is an important out-of-phase coupling of charge-density waves (CDWs), as indicated in Scheme 2.

When interchain interactions are significant, which is the case in polyacene, the bond-length alternation is theoretically predicted to be strongly suppressed.³² The long and short bond lengths of polyacene at the bottom of Scheme 2 were optimized to be 1.424 and 1.391 Å,^{12b} respectively, at the CNDO/2 level of band theory. The optimized bond-length alternation of polyacene is clearly smaller than that of *trans*-polyene; its long and short bond lengths are 1.435 and 1.350 Å,³³ respectively, at the same level of theory. Accordingly, we can neglect C–C bond-length alternation in ladder polymers for qualitative analyses of their electronic structures. Essential orbital interactions in ladder polymers should remain unchanged by this assumption.

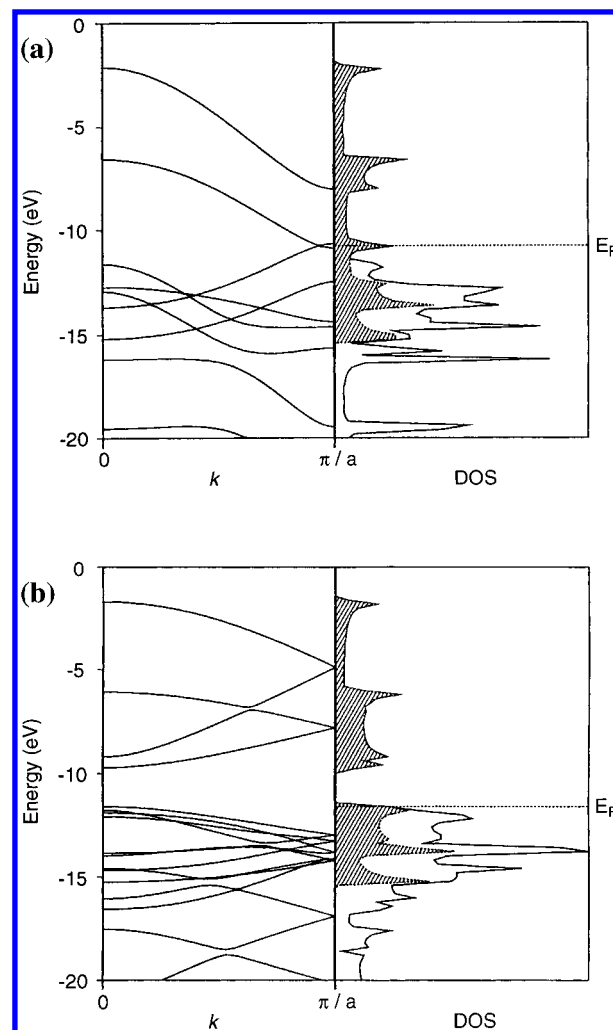


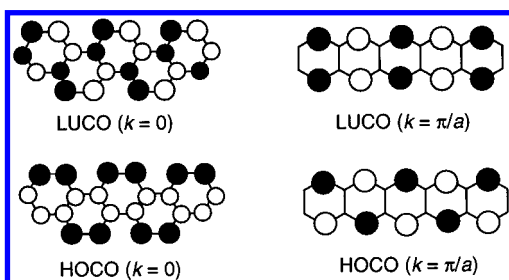
Figure 1. Band structures and density of states (DOS) of (a) polyacene and (b) polyphenanthrene. The dotted lines and shaded areas in the DOSs indicate the Fermi level and the contribution from π bands, respectively. The overlap of the two frontier bands and the finite DOS at the Fermi level in (a) polyacene is due to long-range neighbor interactions in the isodistant model.^{15a}

Results and Discussion

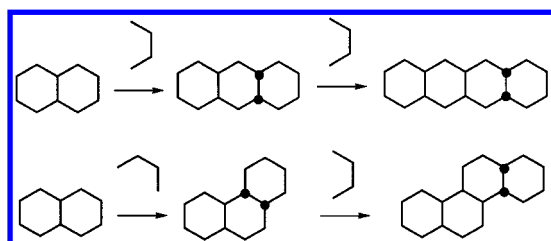
Polyacene and Polyphenanthrene. Let us first make a comparison between polyacene and polyphenanthrene. Polyacene and polyphenanthrene are strikingly different in their edge structures and in their electronic structures. They are supposed to be prototypes of carbon-based ladder polymers and nanosized amorphous carbon materials. It is well-established by various theoretical treatments that polyphenanthrene is energetically more favorable than polyacene.^{21b,23a} The well-known band structure and DOS of polyacene and those of polyphenanthrene are shown in parts a and b of Figure 1, respectively. The shaded area in the DOS indicates the contribution from the π bands, and the dotted line marks the Fermi level (E_F).

As shown in Figure 1a, there is no bandgap in isodistant polyacene, and this would ensure high electrical conductivity if this polymer is prepared. The highest occupied crystal orbital (HOCO) and lowest unoccupied crystal orbital (LUCO) touch each other in the vicinity of the zone edge ($k = \pi/a$). The crossing of the two frontier bands and the finite DOS at the Fermi level shown in Figure 1a is due to long-range neighbor interactions in the isodistant model. If we restrict the lattice summations to second-nearest neighboring interactions, the two bands touch at the zone edge; see the discussion of Kertesz

SCHEME 3



SCHEME 4



and Hoffmann.^{14a} As calculated by Whangbo, Hoffmann, and Woodward,¹¹ this degeneracy is removed when a certain bond-length alternation is introduced into the undistorted structure, as indicated in Scheme 2. Polyacene has been predicted to have an intrinsic bandgap of about 0.3–0.5 eV,^{12b,14b} which is small compared with that of *trans*-polyene (~1.5 eV). The small bond-length alternation and the resultant small bandgap of polyacene are due to a second-order perturbation effect,^{14a,30–32} as mentioned above. Thus, the essential features of the orbital interaction analyses would not be affected by our isodistant models.

In contrast to polyacene, the band structure of polyphenanthrene has not been studied in detail, except for ref 12b. It has

a large bandgap of 2 eV, which is larger than the gap of a single polyene chain, as shown in Figure 1b. The HOCOs and LUCOs for polyphenanthrene and polyacene are indicated in Scheme 3. The HOCO and LUCO of polyacene are of the nonbonding type, and therefore, these are essentially degenerate if we neglect weak interactions between two *trans*-polyene chains within the framework of a nearest-neighbor approximation. On the other hand, the HOCO of polyphenanthrene is derived from the in-phase combination of the HOCOs of two *cis*-polyene chains, and the LUCO of polyphenanthrene from the out-of-phase combination of the LUCOs of two *cis*-polyene chains. Because of the nice interchain orbital interactions, the HOCO and LUCO of polyphenanthrene are greatly stabilized and destabilized, respectively, and its bandgap becomes rather large accordingly.

Anthracene and Phenanthrene. To clarify the remarkable difference in polyacene and polyphenanthrene, we examine the electronic structures of small carbon clusters with different edge structures. For example, the acene-edge group we have investigated includes anthracene and naphthalene and the phenanthrene-edge group phenanthrene and chrysene. We think that the difference between the two types of ladder polymers with different edge structures can be reduced to the characterization of anthracene and phenanthrene. The characterization of the electronic structures of anthracene and phenanthrene is a classical problem in quantum chemistry. Fukui³⁴ and Hosoya^{23a,35} explained the reason why phenanthrene is energetically more stable than anthracene by regarding naphthalene as a starting molecule for construction of the two PAHs. To the best of our knowledge, however, detailed orbital-interaction analyses that are helpful for gaining a better understanding of the contrast between the two PAHs have not yet performed.

Let us look at the difference between anthracene and phenanthrene in terms of orbital interactions. Anthracene and phenanthrene can be theoretically partitioned into naphthalene

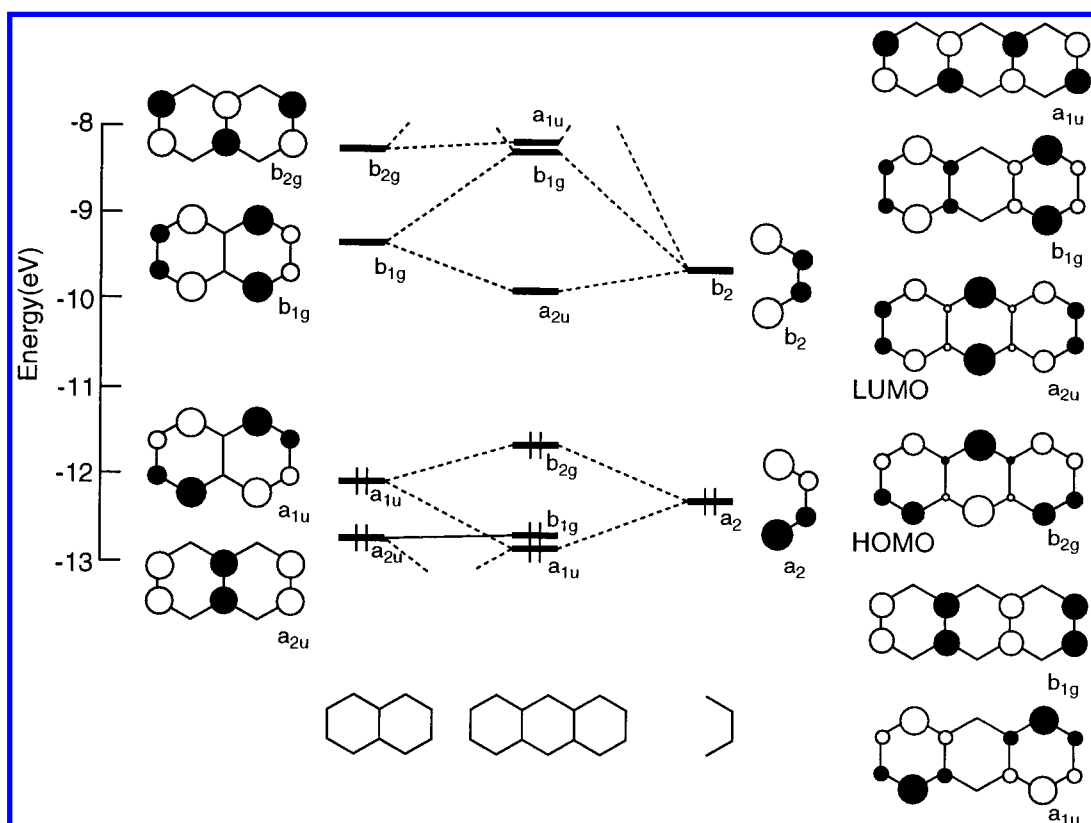


Figure 2. Orbital-interaction diagram for anthracene partitioned into naphthalene and butadiene fragments.

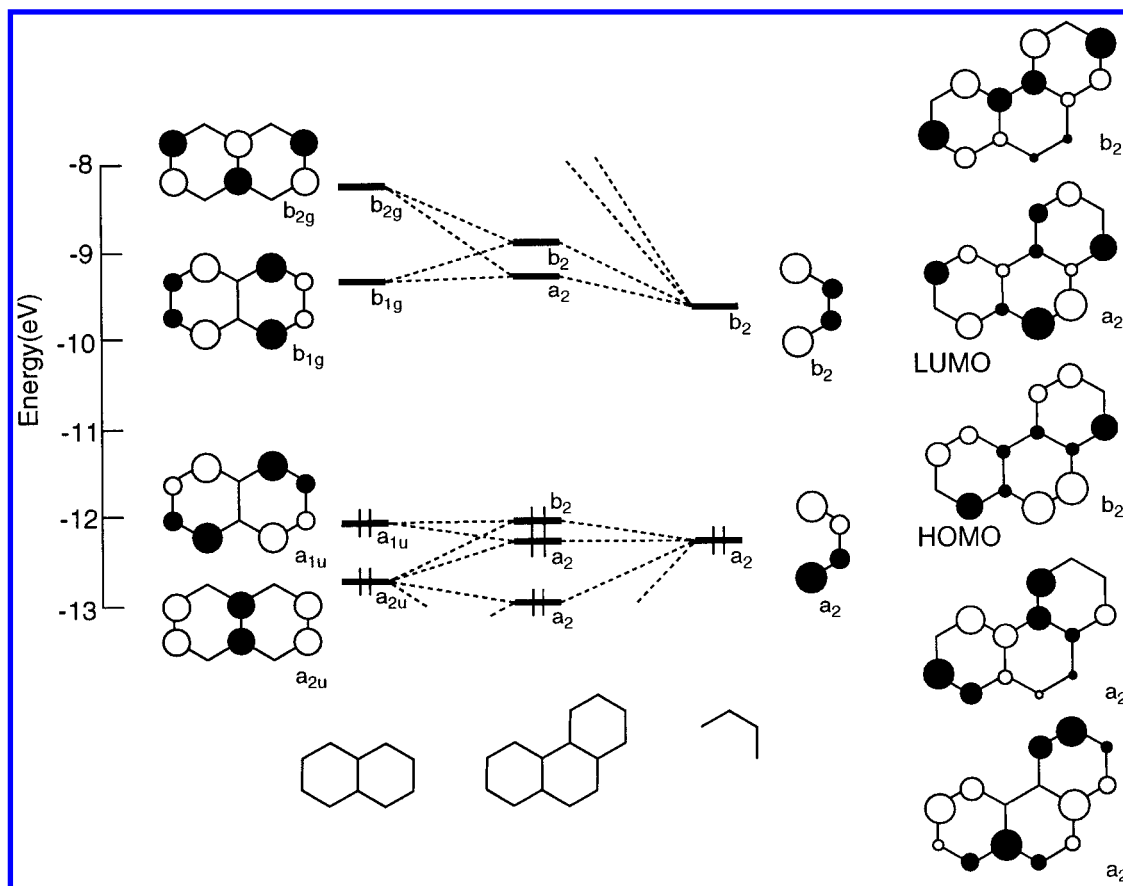


Figure 3. Orbital-interaction diagram for phenanthrene partitioned into naphthalene and butadiene fragments.

and butadiene fragments in different ways, although other partitions are possible. Anthracene is derived by connecting the two terminal carbons of butadiene to the 2 and 3 sites of naphthalene, and phenanthrene by connecting the two terminal carbons of butadiene to the 1 and 2 sites of naphthalene, as indicated in Scheme 4. Naphthacene and chrysene can be constructed in similar ways. We apply the useful FMO method to the characterization of the electronic structures of anthracene and phenanthrene.

We show an orbital-interaction diagram for anthracene in Figure 2, in which σ orbitals are neglected. It is essential to note that the b_{2g} HOMO and a_{2u} LUMO of anthracene are closely lying compared with the HOMOs and LUMOs of the naphthalene and butadiene fragments. We consider the reason why the HOMO–LUMO gap of anthracene becomes small. As shown in Figure 2, the a_{1u} HOMO of naphthalene and the a_2 HOMO of butadiene interact nicely at the connecting sites (2 and 3 sites of naphthalene) so that the in-phase combination b_{1g} is pushed down and the out-of-phase counterpart b_{2g} , the HOMO of anthracene, is pushed up. Moreover, since the b_{1g} LUMO of naphthalene and the b_2 LUMO of butadiene also interact nicely, the in-phase combination a_{2u} , the LUMO of anthracene, is pushed down and the out-of-phase combination b_{1g} is pushed up. As a consequence, the HOMO–LUMO gap of anthracene becomes small.

On the other hand, the HOMO–LUMO gap of phenanthrene is rather large, as shown in Figure 3. The FMO analyses for phenanthrene are strikingly different from those for anthracene. The a_{1u} HOMO of naphthalene and the a_2 HOMO of butadiene have no good interaction at the connecting sites (1 and 2 sites of naphthalene), but the a_{1u} HOMO of naphthalene and the b_2 LUMO of butadiene have a good interaction due to their orbital symmetries. The latter in-phase HOMO–LUMO interaction

between the fragments would importantly give rise to electron delocalization at the connecting sites,³⁴ which will lead to stabilization of this molecule, phenanthrene. Also, the b_{1g} LUMO of naphthalene and the b_2 LUMO of butadiene have no interaction at the connecting sites, but the b_{1g} LUMO of naphthalene and the a_2 HOMO of butadiene have a good interaction that would also lead to electron delocalization at the connecting sites. As a consequence, the HOMO of phenanthrene is stabilized and the LUMO of phenanthrene is destabilized. Thus, the HOMO–LUMO gap of phenanthrene becomes larger than that of anthracene.

Let us further look at the difference between naphthacene and chrysene. The molecular orbitals of naphthacene and chrysene are constructed from those of anthracene and butadiene fragments in similar ways as in Figures 2 and 3. We show the orbital interaction diagrams for naphthacene and chrysene in Figures 4 and 5, respectively. For these compounds, we do not repeat similar discussions for anthracene and phenanthrene. Because of significant orbital symmetries, the HOMO of naphthacene is destabilized and the LUMO of naphthacene is stabilized more than in anthracene, and thus the HOMO–LUMO gap becomes smaller than that of anthracene, as can be seen in Figure 4. On the other hand, the HOMO–LUMO gap of chrysene is almost unchanged from that of phenanthrene, owing to orbital symmetries, as can be seen in Figure 5.

We think that the FMO method can be applied to the characterization of the aromaticity of anthracene and phenanthrene, as shown in Figures 2 and 3. This method clearly explains how the HOMO–LUMO energy gap, which may serve as an index of stability and reactivity,³⁶ depends on the edge structures of the PAHs. Anthracene behaves as a soft base and acid and phenanthrene as a hard base and acid. It is likely to be interesting to reconsider aromaticity and antiaromaticity of

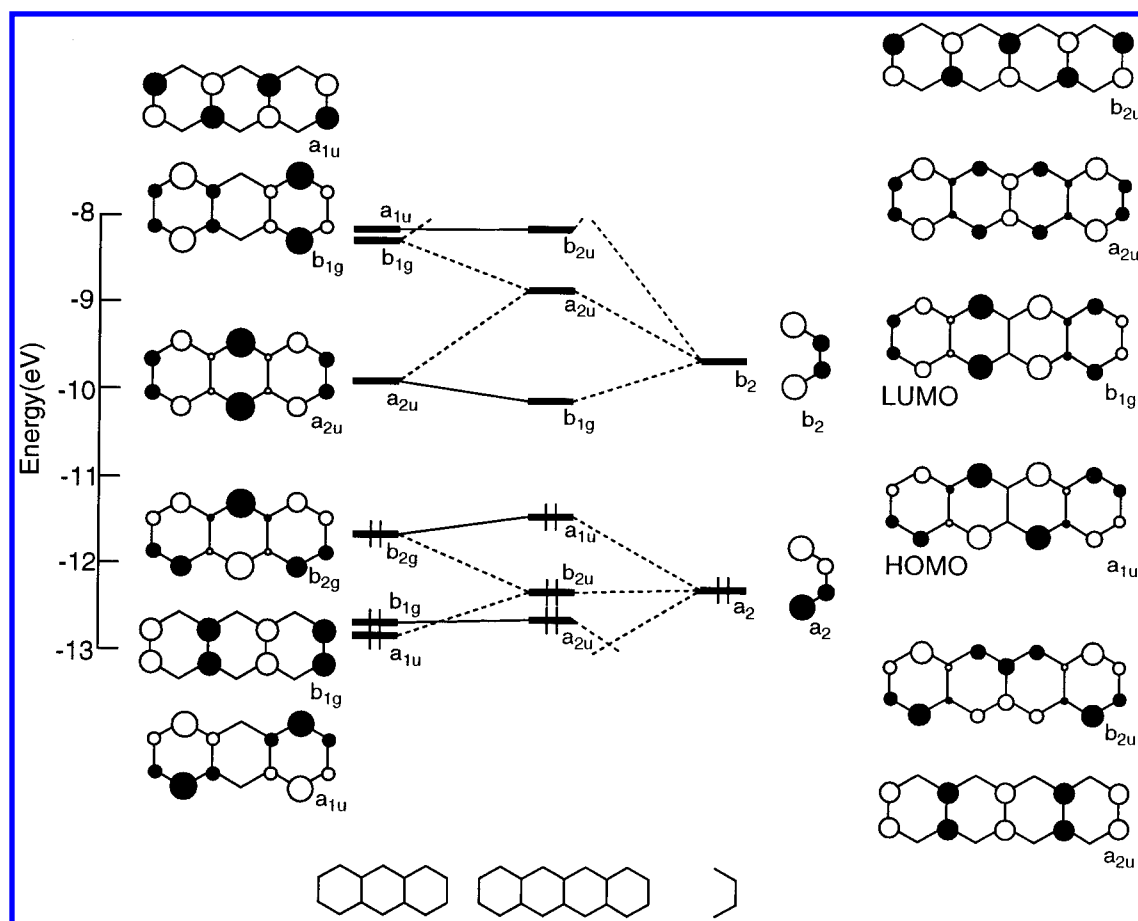


Figure 4. Orbital-interaction diagram for naphthalene partitioned into anthracene and butadiene fragments.

PAHs from the viewpoint of the recent concept of hard and soft acids and bases.^{36,37}

Ladder Polymers with Phenanthrene Edge. It is a main subject in this paper to characterize the ladder polymers with a phenanthrene-edge structure. When increasing the chain width of ladder polymers, the bandgap approaches zero, as shown in Figure 6, but the acene-edge series and phenanthrene-edge series show quite different n dependencies, in which n is the number of polyene chains included. The bandgap of the acene-edge series decreases very rapidly with an increase in chain width, although a small gap, due to a higher-order perturbational effect, always occurs.^{14a} On the other hand, the gap of the phenanthrene-edge series approaches zero very slowly with increasing n in an oscillating manner, as indicated previously in ref 12e.

Polyacene and polyphenanthrene can be viewed as interacting *trans*-polyene chains and *cis*-polyene chains, respectively; we call the polyacene series PA(n) and the polyphenanthrene series PPh(n). Tanaka, Yamabe, and their co-workers^{12e} calculated the bandgaps of the PA(n) and PPh(n) series within the framework of the Hückel method and showed that the gap in the PA(n) series decreases very rapidly to zero. The bandgap of PA(n) is actually 0 when n is greater than 3 even if bond-length alternation is taken into account. On the other hand, the behavior of the calculated gap of the PPh(n) series is remarkably different from that of the PA(n) series. Topological factors governing the bandgap of ladder polymers were analyzed by Hosoya and co-workers.³⁸ One of our main interests in this paper is to characterize in terms of orbital interactions the electronic structures of PPh(n) rather than PA(n). The bandgap of PPh(n) computed with the extended Hückel method is shown as a function of n in Figure 7. The gap of PPh(n) slowly

approaches zero (graphite's value) with a behavior that has a periodicity of 3.^{12e}

The behavior of the periodicity is similar to that of carbon nanotubes where the graphene strip is rolled and the edged joined to make a tube.³⁹ To understand the interesting periodicity in the calculated bandgap of PPh(n), we analyzed the frontier crystal orbitals of the PPh(n) series. We show the HOCOs and LUCOs of PPh(1)–PPh(6) (at $k = 0$) in Figure 8. From closer inspection, we found a similar periodic change in the HOCO and LUCO of the PPh(n) series. On the basis of the frontier crystal-orbital patterns, we can classify the PPh(n) series into three subgroups: small-gap (metallic) group (PPh(1), PPh(4), ..., PPh($3m + 1$), ...), large-gap group (PPh(2), PPh(5), ..., PPh($3m + 2$), ...), and medium-gap group (PPh(3), PPh(6), ..., PPh($3m$), ...), in which $m = 0, 1, 2, \dots$. Let us look at the correlation between the periodic behavior of the bandgap and the interchain interactions in the frontier orbitals.

In the metallic group, there are striking nodes along the chain axis, as shown in the HOCO and LUCO of PPh(4) in Figure 8. The HOCO and LUCO of PPh(4) are composed of the HOCOs and LUCOs of single polyene chains PPh(1), respectively, and there is almost no orbital interaction between the two chains due to the significant nodal properties. That is, the frontier orbitals of the PPh($3m + 1$) subgroup are of nonbonding type along the polymer width. Therefore, the levels of the HOCO and LUCO remain almost unchanged from those of a single polyene chain PPh(1). Distant interchain interactions, which are strongly antibonding in the HOCO as we can see in PPh(4), would decrease the bandgap with increasing m . It is important to note that there are distinct conduction pathways in this group, as in carbon nanotubes.³⁹ Thus, we think that

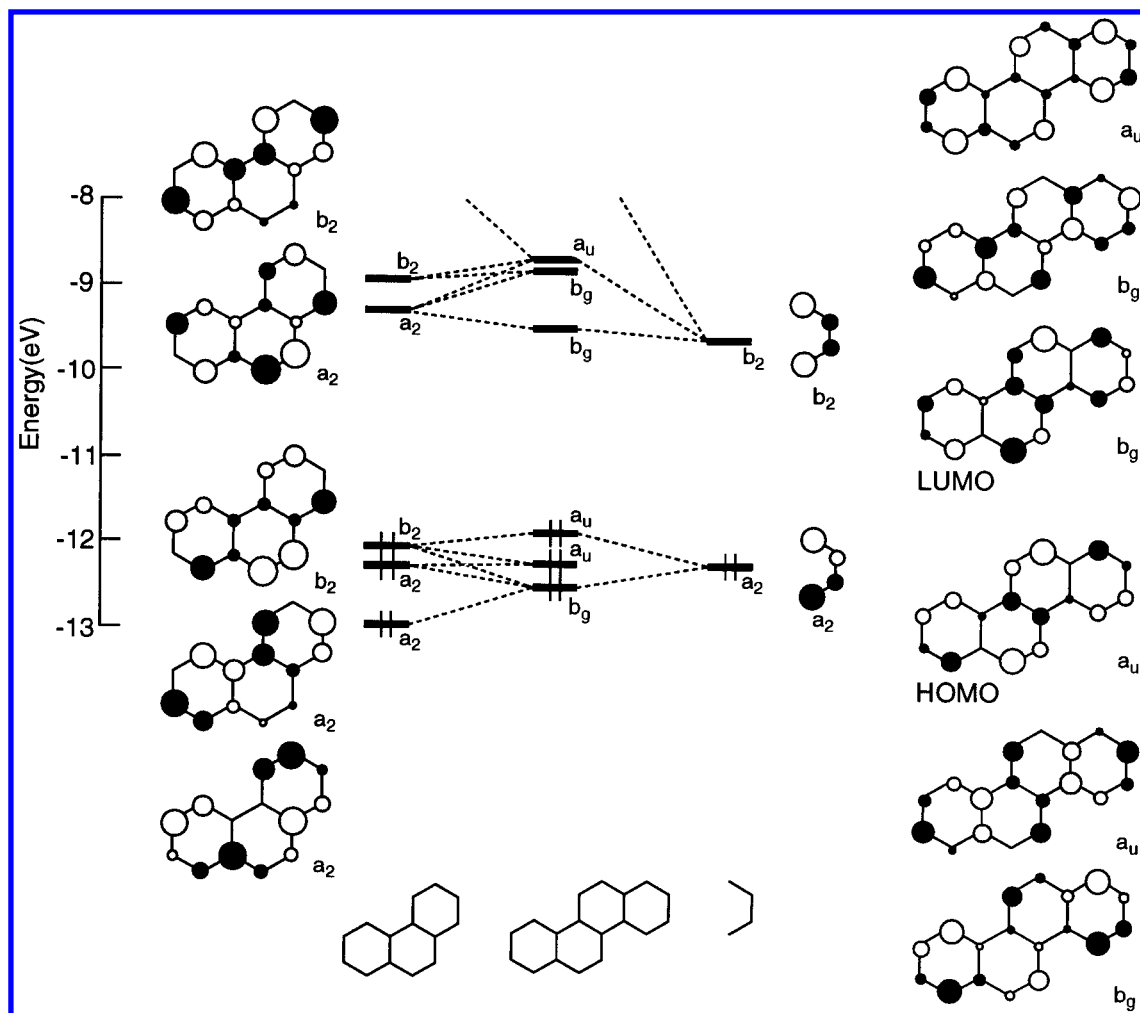


Figure 5. Orbital-interaction diagram for chrysene, partitioned into phenanthrene and butadiene fragments.

the $\text{PPh}(3m + 1)$ subgroup is an interesting synthetic target for a small-gap polymer material. There are no orbital coefficients in the connecting regions. This can be viewed as a “fading-away” phenomenon⁴⁰ due to mixing between the frontier orbitals and the higher or lower orbitals.

In the large-gap group, the interchain interactions in the HOCO and LUCO are significant, as shown in the HOCO and LUCO of $\text{PPh}(2)$ and $\text{PPh}(5)$ in Figure 8. As a consequence, the HOCO is greatly stabilized, owing to the in-phase combination of the HOCOs of single polyene chains, and the LUCO is destabilized, owing to the out-of-phase combination of the LUCOs of single polyene chains. Thus, the bandgap of the $\text{PPh}(3m + 2)$ subgroup becomes rather large, and we expect this subgroup to be energetically most stable in the $\text{PPh}(n)$ series. The $\text{PPh}(3m + 2)$ subgroup is likely to have remarkable aromaticity compared with other groups. On the basis of the calculated bandgap, only $\text{PPh}(2)$, i.e., polyphenanthrene, is expected to absorb visible light and to exhibit color. Other polymers in the $\text{PPh}(n)$ series should be black, we think. Thus, $\text{PPh}(2)$ may be interesting for its application to the solar cell.

In the medium-gap group, interchain interactions are not significant but still exist. It is notable that the frontier orbital patterns of this group are quite different from those of other groups. As shown in the HOCOs of $\text{PPh}(3)$ and $\text{PPh}(6)$ in Figure 8, they are composed of the in-phase coupling of the LUCOs of single polyene chains. We can see a small contribution of a higher crystal orbital in the connecting region. Moreover, the LUCOs of $\text{PPh}(3)$ and $\text{PPh}(6)$ are composed of the out-of-phase coupling of the HOCOs of single chains. It is

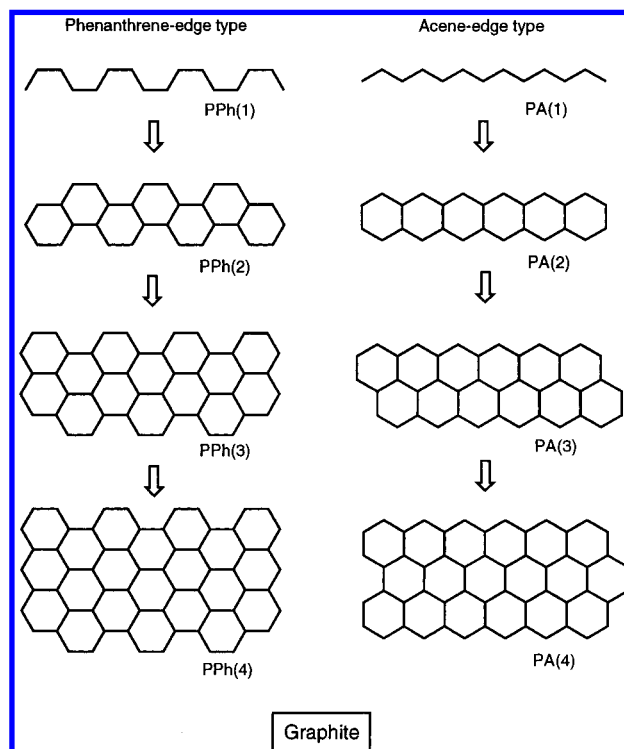


Figure 6. Carbon-based ladder polymers with acene- and phenanthrene-edge structures. The polyacene series, $\text{PA}(n)$, can be constructed from connecting *trans*-polyene chains and the polyphenanthrene series, $\text{PPh}(n)$, from connecting *cis*-polyene chains.

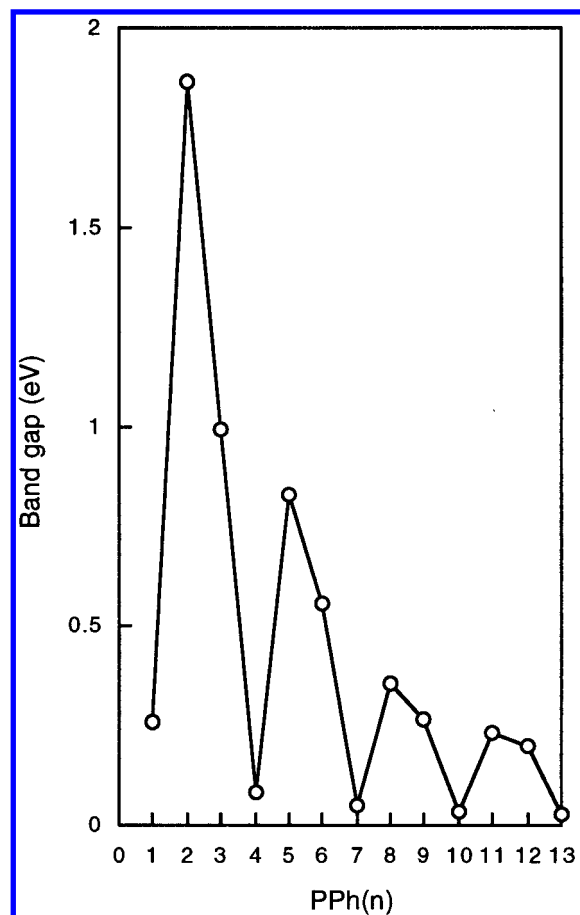
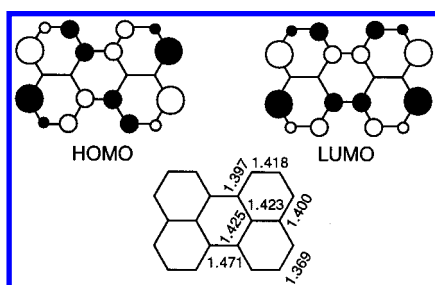


Figure 7. Bandgap of the PPh(*n*) series as a function of *n*, the number of *cis*-polyene chains.

SCHEME 5



also important to note that a lower crystal orbital plays a role in the connecting region of the LUCOs. PPh(3*m*) is thus different from other subgroups in the way of orbital mixing. Thus, the HOCO and LUCO are a little stabilized and destabilized, respectively. The bandgap of PPh(3*m*) subgroup becomes medium accordingly.

These frontier orbital patterns readily predict that there would appear trans-cisoid-edge structures in this group, in remarkable contrast to other groups. This is an interesting consequence because the trans-cisoid form corresponds to an excited-state structure for a *cis*-polyene chain. Moreover, in this subgroup, the amplitude of the frontier orbitals is not significant in the phenanthrene-edge regions, which is also different from other subgroups. We can find similar frontier orbital patterns in perylene, as shown in Scheme 5. The HOMO and LUMO of perylene are quite different from those of phenanthrene especially in their bay regions. The HOMO of perylene can be viewed as the out-of-phase combination of the HOMO of naphthalene and the LUMO of perylene as the in-phase combination of the LUMO of naphthalene. The observed bond

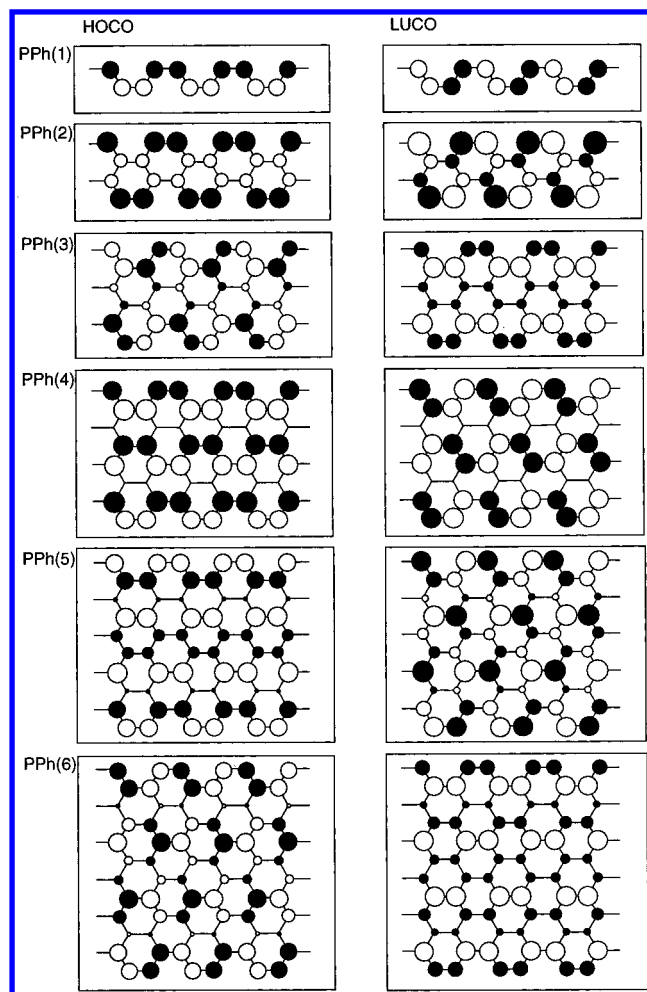


Figure 8. HOCOs (highest occupied crystal orbital) and LUCOs (lowest unoccupied crystal orbital) of PPh(*n*).

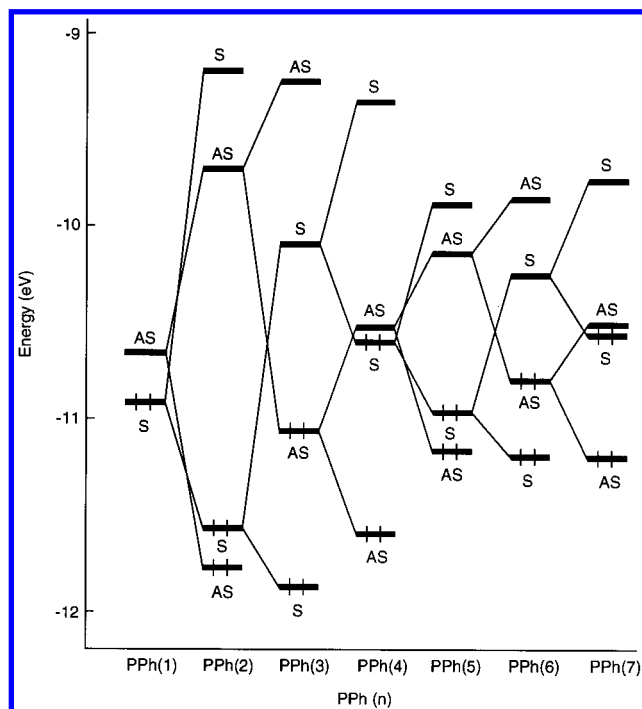
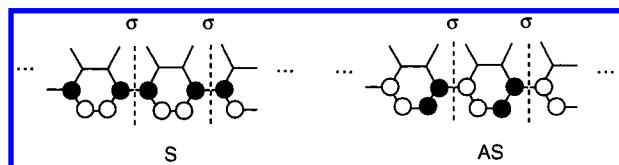


Figure 9. Schematic representation of the evolution of the frontier crystal orbitals of PPh(*n*), in which *n* is the number of *cis*-polyene chains included. "S" means a symmetric orbital with respect to the mirror plane (σ) at the bay region of the edge and "AS" an antisymmetric orbital, as indicated in Scheme 6.

SCHEME 6



lengths, indicated in the bottom of Scheme 5 (from ref 22c), are qualitatively consistent with the HOMO pattern.

Let us finally look at the way that the bandgap and the symmetry of the frontier crystal orbitals of PPh(*n*) exhibit such oscillating behavior. In Figure 9, the evolution of the crystal orbital properties of PPh(*n*) at the zone center (*k* = 0) is shown as a function of *n*. Here, "S" means a symmetric orbital with respect to the mirror plane (σ) at the center of the bay of the edge and "AS" an antisymmetric orbital, as shown below in Scheme 6.

The crystal orbitals of PPh(*n* + 1) are composed of interactions of the fragment crystal orbitals of PPh(*n*) and PPh(1). For example, the HOCO of PPh(1) would split into two in constructing PPh(2), the in-phase combination being stabilized and the out-of-phase one destabilized, as shown in Figure 9. In the case of PPh(3), in which the symmetries of the HOCO and LUCO are exchanged, the stabilized part derived from the LUCO of PPh(2) lies between the stabilized and destabilized parts from the HOCO of PPh(2), and the destabilized part from the HOCO of PPh(2) lies between the stabilized and destabilized parts from the LUCO of PPh(2). As mentioned above, there are small orbital mixings of higher and lower crystal orbitals especially in the connecting region of PPh(3*m*). The higher (lower) orbital plays a role for the stabilization (destabilization) of the HOCO (LUCO) of PPh(3). In this way, the symmetries of the HOCO and LUCO are exchanged in PPh(3) and PPh(3*m*). In PPh(4), and furthermore in PPh(3*m* + 1), a reversal of the symmetries of the HOCO and LUCO should occur in a similar way. Therefore, the symmetries of the HOCO and LUCO are exchanged in a three-periodic manner and there are three subgroups for the energy gap of PPh(*n*) series.

Conclusions

We have discussed the electronic structures of carbon-based ladder polymers and PAHs with two distinct "acene-edge" (or zigzag) and "phenanthrene-edge" (or arm-chair) structures. The difference between polyacene and polyphenanthrene can be derived from a detailed orbital interaction analysis of anthracene and phenanthrene. Anthracene and phenanthrene can be theoretically partitioned into naphthalene and butadiene fragments. In constructing anthracene, the a_{1u} HOMO of naphthalene and the a_2 HOMO of butadiene interact nicely at the connecting sites (2 and 3 sites of naphthalene) so that the out-of-phase coupling b_{2g} , the HOMO of anthracene, is significantly pushed up. Moreover, since the b_{1g} LUMO of naphthalene and the b_2 LUMO of butadiene also interact nicely, the in-phase combination a_{2u} , the LUMO of anthracene, is pushed down. As a consequence, the HOMO–LUMO gap of anthracene becomes small. On the other hand, in constructing phenanthrene, the a_{1u} HOMO of naphthalene and the a_2 HOMO of butadiene have no good interaction at the connecting sites (1 and 2 sites of naphthalene). Also, the b_{1g} LUMO of naphthalene and the b_2 LUMO of butadiene have no interaction at the connecting sites. The HOMO and LUMO of phenanthrene are left unchanged from those of naphthalene. The difference between anthracene and phenanthrene will tell us the reason why the energy gap of ladder polymers depends on their edge structures.

We shed special light on the oscillation of the bandgap in the ladder polymers with phenanthrene-edge structure, PPh(*n*). With an increase in width of the ladder polymers, the bandgap of PPh(*n*) approaches zero (graphite's value) in an oscillating manner, in contrast to the bandgap of PA(*n*) that decreases very rapidly. The PPh(*n*) series can be classified into three subgroups: small-gap (metallic) PPh(3*m* + 1), large-gap PPh(3*m* + 2), and medium-gap PPh(3*m*). The oscillating behavior in the bandgap of the three subgroups has been explained from the viewpoint of interchain interactions in the frontier crystal orbitals. From the calculated bandgap, only PPh(2), i.e., polyphenanthrene, would absorb visible light, and thus, its application to solar cell is likely to be interesting.

Acknowledgment. We are grateful to a Grant-in-Aid for Scientific Research from the Ministry of Education, Science, and Culture of Japan for its support of this work. Thanks are also due to "Research for the Future" Program by the Japan Society for the Promotion of Science (JSPS-RFTF96P00206) for financial support.

References and Notes

- (1) (a) Yata, S.; Kinoshita, H.; Komori, M.; Ando, N.; Kashiwamura, T.; Harada, T.; Tanaka, K.; Yamabe, T. *Synth. Met.* **1994**, *62*, 153. (b) Yata, S.; Hato, Y.; Kinoshita, H.; Ando, N.; Anekawa, A.; Hashimoto, T.; Yamaguchi, M.; Tanaka, K.; Yamabe, T. *Synth. Met.* **1995**, *73*, 273.
- (2) (a) Sato, K.; Noguchi, M.; Demachi, A.; Oki, N.; Endo, M. *Science* **1994**, *264*, 556. (b) Matthew, M. J.; Bi, X. X.; Dresselhaus, M. S.; Endo, M.; Takahashi, T. *Appl. Phys. Lett.* **1996**, *68*, 1078.
- (3) (a) Dahn, J. R.; Zheng, T.; Liu, Y.; Xue, J. S. *Science* **1995**, *270*, 590. (b) Zheng, T.; Liu, Y.; Fuller, E. W.; Tseng, S.; von Sacken, U.; Dahn, J. R. *J. Electrochem. Soc.* **1995**, *142*, 2581. (c) Liu, Y.; Xue, J. S.; Zheng, T.; Dahn, J. R. *Carbon* **1996**, *34*, 193.
- (4) Gerouki, A.; Goldner, M. A.; Goldner, R. B.; Haas, T. E.; Liu, T. Y.; Slaven, S. *J. Electrochem. Soc.* **1996**, *143*, L262.
- (5) Novák, P.; Müller, K.; Santhanam, K. S. V. *Chem. Rev.* **1997**, *97*, 207.
- (6) (a) Hess, B. A., Jr.; Schaad, L. J. *J. Am. Chem. Soc.* **1971**, *93*, 305. (b) Hess, B. A., Jr.; Schaad, L. J. *J. Org. Chem.* **1971**, *36*, 3418.
- (7) (a) Herndon, W. C. *Tetrahedron* **1973**, *29*, 3. (b) Herndon, W. C.; Ellzey, M. L. *J. Am. Chem. Soc.* **1974**, *96*, 6631. (c) Herndon, W. C. *J. Org. Chem.* **1975**, *40*, 3583. (d) Herndon, W. C. *J. Org. Chem.* **1981**, *46*, 2119. (e) Herndon, W. C. *Tetrahedron* **1982**, *38*, 1389.
- (8) (a) Stein, S. E.; Brown, R. L. *Carbon* **1985**, *23*, 105. (b) Stein, S. E.; Brown, R. L. *J. Am. Chem. Soc.* **1987**, *109*, 3721. (c) Chen, R. H.; Kafafi, S. A.; Stein, S. E. *J. Am. Chem. Soc.* **1989**, *111*, 1418. (d) Stein, S. E.; Brown, R. L. *J. Am. Chem. Soc.* **1991**, *113*, 787. (e) Stein, S. E. *Acc. Chem. Res.* **1991**, *24*, 350.
- (9) Klimkåns, A.; Larsson, S. *Chem. Phys.* **1994**, *189*, 25.
- (10) (a) Yamabe, T.; Yamashita, S.; Yamabe, H.; Fukui, K.; Tanaka, K. *Collect. Czech. Chem. Commun.* **1988**, *53*, 1881. (b) Yoshizawa, K.; Okahara, K.; Sato, T.; Tanaka, K.; Yamabe, T. *Carbon* **1994**, *32*, 1517.
- (11) Whangbo, M.-H.; Hoffmann, R.; Woodward, R. B. *Proc. R. Soc. London* **1979**, *A366*, 23.
- (12) (a) Yamabe, T.; Tanaka, K.; Ohzeki, K.; Yata, S. *Solid State Commun.* **1982**, *44*, 823. (b) Tanaka, K.; Ohzeki, K.; Nankai, S.; Yamabe, T.; Shirakawa, H. *J. Phys. Chem. Solid* **1983**, *44*, 1069. (c) Tanaka, K.; Ueda, K.; Koike, T.; Yamabe, T. *Solid State Commun.* **1984**, *51*, 943. (d) Tanaka, K.; Koike, T.; Ueda, K.; Ohzeki, K.; Yamabe, T. *Synth. Met.* **1985**, *11*, 61. (e) Tanaka, K.; Yamashita, S.; Yamabe, H.; Yamabe, T. *Synth. Met.* **1987**, *17*, 143. (f) Tanaka, K.; Yamanaka, S.; Ueda, K.; Takeda, S.; Yamabe, T. *Synth. Met.* **1987**, *20*, 333. (g) Tanaka, K.; Murashima, M.; Yamabe, T. *Synth. Met.* **1988**, *24*, 371.
- (13) (a) Brédas, J. L.; Chance, R. R.; Baughman, R. H.; Silbey, R. J. *Chem. Phys.* **1982**, *76*, 3673. (b) Boudreaux, D. S.; Chance, R. R.; Elsenbaumer, R. L.; Frommer, J. E.; Brédas, J. L. *Phys. Rev.* **1985**, *B31*, 652. (c) Brédas, J. L.; Baughman, R. H. *J. Chem. Phys.* **1985**, *83*, 1316. (d) Toussaint, J. M.; Brédas, J. L. *Synth. Met.* **1992**, *46*, 325.
- (14) (a) Kertesz, M.; Hoffmann, R. *Solid State Commun.* **1983**, *47*, 97. (b) Lee, Y. S.; Kertesz, M. *J. Chem. Phys.* **1988**, *2609*. (c) Kertesz, M.; Lee, Y. S.; Stewart, J. J. P. *Int. J. Quantum Chem.* **1989**, *35*, 305. (d) Hong, S. Y.; Kertesz, M.; Lee, Y. S.; Kim, O.-K. *Chem. Mater.* **1992**, *4*, 378. (e) Kertesz, M. *Macromolecules* **1995**, *28*, 1475. (f) Kertesz, M.; Ashertehrani, A. *Macromolecules* **1996**, *29*, 940.

- (15) (a) Tyutyulkov, N.; Tadjer, A.; Minsheva, I. *Synth. Met.* **1990**, *38*, 313. (b) Baumgarten, M.; Karabunarliev, S.; Koch, K.-H.; Müllen, K.; Tyutyulkov, N. *Synth. Met.* **1992**, *47*, 21.
- (16) (a) Nakada, K.; Fujita, M.; Dresselhaus, G.; Dresselhaus, M. S. *Phys. Rev.* **1996**, *B54*, 17954. (b) Fujita, M.; Wakabayashi, K.; Nakada, K.; Kusakabe, K. *J. Phys. Soc. Jpn.* **1996**, *65*, 1920.
- (17) (a) Quante, H.; Müllen, K. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1323. (b) Müller, M.; Mauermann-Düll, H.; Wagner, M.; Enkelmann, V.; Müllen, K. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1583. (c) Müller, M.; Petersen, J.; Strohmaier, R.; Günther, C.; Karl, N.; Müllen, K. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 886. (d) Holtrup, F. O.; Müller, G. R. T.; Quante, H.; Feyter, S. D.; de Schryver, F. C.; Müllen, K. *Chem. Eur. J.* **1997**, *3*, 219.
- (18) Goddard, R.; Haenel, M. W.; Herndon, W. C.; Krüger, C.; Zander, M. *J. Am. Chem. Soc.* **1995**, *117*, 30.
- (19) (a) Mallory, F. B.; Butler, K. E.; Evans, A. C.; Mallory, C. W. *Tetrahedron Lett.* **1996**, *40*, 7173. (b) Mallory, F. B.; Butler, K. E.; Evans, A. C.; Brondyke, E. J.; Mallory, C. W.; Yang, C.; Ellenstein, A. *J. Am. Chem. Soc.* **1997**, *119*, 2119.
- (20) Roncali, J. *Chem. Rev. (Washington, D.C.)* **1997**, *97*, 173.
- (21) (a) Clar, E. *Polycyclic Hydrocarbons*; Academic Press: London, 1964. (b) Clar, E. *The Aromatic Sextet*; Wiley: London, 1972.
- (22) (a) Dewar, M. J. S.; Gleicher, G. J. *J. Am. Chem. Soc.* **1965**, *87*, 685. (b) Dewar, M. J. S.; de Llano, C. *J. Am. Chem. Soc.* **1969**, *91*, 789. (c) Dewar, M. J. S. *The Molecular Orbital Theory of Organic Chemistry*; McGraw-Hill: New York, 1969.
- (23) (a) Hosoya, H.; Yamaguchi, T. *Tetrahedron Lett.* **1975**, *52*, 4659. (b) Hosoya, H.; Hosoi, K.; Gutman, I. *Theor. Chim. Acta* **1975**, *38*, 37.
- (24) (a) Randić, M. *Chem. Phys. Lett.* **1976**, *38*, 68. (b) Randić, M. *J. Am. Chem. Soc.* **1977**, *99*, 444.
- (25) (a) Aihara, J. *J. Am. Chem. Soc.* **1976**, *98*, 2750. (b) Aihara, J. *Pure Appl. Chem.* **1982**, *54*, 1115.
- (26) See the following, for example. Albright, T. A.; Burdett, J. K.; Whangbo, M.-H. *Orbital Interactions in Chemistry*; Wiley: New York, 1985.
- (27) (a) Hoffmann, R. *J. Chem. Phys.* **1963**, *39*, 1397. (b) Hoffmann, R.; Lipscomb, W. N. *J. Chem. Phys.* **1962**, *36*, 2179; **1962**, *37*, 2872.
- (28) Landrum, G.; YaeHMOP (Yet Another Extended Hückel Molecular Orbital Package); Cornell University: Ithaca, NY, 1995.
- (29) Peierls, R. E. *Quantum Theory of Solids*; Oxford University: Oxford, 1955.
- (30) Whangbo, M.-H. In *Crystal Chemistry and Properties of Materials with Quasi-One-Dimensional Structures*; Rouxel, J., Ed.; Reidel: Dordrecht, 1986; p 27.
- (31) Yoshizawa, K.; Hoffmann, R. *J. Chem. Phys.* **1995**, *103*, 2126.
- (32) Aoki, Y.; Imamura, A. *J. Chem. Phys.* **1995**, *103*, 9726.
- (33) Yamabe, T.; Tanaka, K.; Terama-e, H.; Fukui, K.; Imamura, A.; Shirakawa, H.; Ikeda, S. *J. Phys. C: Solid State Phys.* **1979**, *12*, L257.
- (34) Fukui, K. *Science* **1982**, *218*, 747, and references therein.
- (35) Hosoya, H. In *Chemistry of Novel Aromatic Systems* (in Japanese); Chemical Society of Japan, Ed.; Gakkai Shuppan: Tokyo, 1977; p 23.
- (36) Pearson, R. G. *J. Chem. Educ.* **1987**, *64*, 561.
- (37) Parr, R. G.; Yang, W. *Density Functional Theory of Atoms and Molecules*; Oxford University: Oxford, 1989.
- (38) (a) Hosoya, H.; Kumazaki, H.; Chida, K.; Ohuchi, M.; Gao, Y.-D. *Pure Appl. Chem.* **1990**, *62*, 445. (b) Gao, Y.-D.; Kumazaki, H.; Terai, J.; Chida, K.; Hosoya, H. *J. Math. Chem.* **1993**, *12*, 279.
- (39) (a) Hamada, N.; Sawada, S.; Oshiyama, A. *Phys. Rev. Lett.* **1992**, *68*, 1579. (b) Tanaka, K.; Okahara, K.; Okada, M.; Yamabe, T. *Chem. Phys. Lett.* **1992**, *191*, 469. (c) Saito, R.; Fujita, M.; Dresselhaus, G.; Dresselhaus, M. S. *Appl. Phys. Lett.* **1992**, *60*, 2204.
- (40) Woodward, R. B.; Hoffmann, R. *The Conservation of Orbital Symmetry*; Verlag Chemie GmbH: Weinheim, 1970.