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Direct and indirect band gap types in one-dimensional conjugated or stacked organic materials*

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Abstract. Whether a semiconductor has a direct or an indirect band gap is important in determining physical properties such as photoconductivity and electroluminescence. For one-dimensional conjugated polymeric semiconductors, as well as organic molecular crystals, we show how the band gap type (direct or indirect) is determined by the shapes of the HOMO and the LUMO of constituent monomeric conjugated molecules. The connectivity of the monomer units, and the topology of orbital interaction determine the band gap type. Pairing symmetry in the π electronic system of even alternant hydrocarbons allows the immediate prediction of the band gap type, direct or indirect, by examining only the structures of the monomer units and their connectivity in polymers or molecular stacks.

Key words: Organic semiconductors – Band gap types – Molecular orbital theory – Photoconductivity – Electroluminescence

1 Introduction

Characteristic of semiconducting and insulating materials is a band gap between valence and conduction bands. The band gap can be classified as direct or indirect – a band gap is said to be "direct" when the energy minimum (the bottom) of the conduction band lies directly above the energy maximum (the top) of the valence band in reciprocal **k**-space (Fig. 1a) [1, 2].[1] Otherwise, we call it an "indirect" band gap (Fig. 1b). The crystal orbitals at the top of the valence band and at the bottom of the conduction band have the same wave vector in a direct band gap solid, but different wave vectors in an indirect band gap material.

Whether the gap is direct or indirect is important in the application of inorganic semiconductors (such as Si, Ge and GaAs) to photoconduction and electroluminescence [3–10], because it is one of the major factors that determines the efficiency of these processes. In photoconductive materials, electrons and holes are created by absorption of light. Some of the electrons and holes may recombine through nonradiative or radiative process, while the reminder may propagate through the lattice, thereby resulting in electrical current flow. For electroluminescence, electrons and holes are injected at the ends of the samples, and flow toward the opposite end under an electric potential gradient. When the electrons and holes pass by each other, they can recombine through a nonradiative or a radiative process, as in the case of photoconduction. For maximum electroluminescence efficiency, therefore, it is desirable to maximize radiative recombination processes. However, the opposite characteristic is of value in the case of photoconduction, where any recombination processes need be minimized.

While nonradiative processes are controlled by the concentration of the recombination centers such as defect and impurity sites, the radiative process is governed by an optical selection rule. Putting aside the possibility of exciton formation [11, 12], the photogenerated or injected electrons and holes are located at the bottom of the conduction band and at the top of the valence band, respectively. When electrons and holes recombine radiatively, an optical transition occurs between the crystal orbitals at the bottom of the conduction band and at the top of the valence band (Fig. 2a). For this transition to be allowed, conservation of momentum as well as of energy needs to be satisfied. Since the light normally of interest to us, infrared or UV-visible, has a very long wavelength compared to the unit cell length of the solids, its momentum, $\mathbf{k}_{h\nu}$ can be neglected. Hence, for an allowed transition it is essential to satisfy $\Delta\mathbf{k} = \mathbf{k}_{\text{electron}} - \mathbf{k}_{\text{hole}} = \mathbf{k}_{h\nu} \approx 0$. In other words, radiative recombination of electrons and holes is forbidden in semiconductors with an indirect band gap. For solids

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[1] ε_F is marked at the top of the valence band throughout this paper, so as to indicate the highest occupied crystal orbital. A positioning more consistent with convention would be between the valence and the conduction band

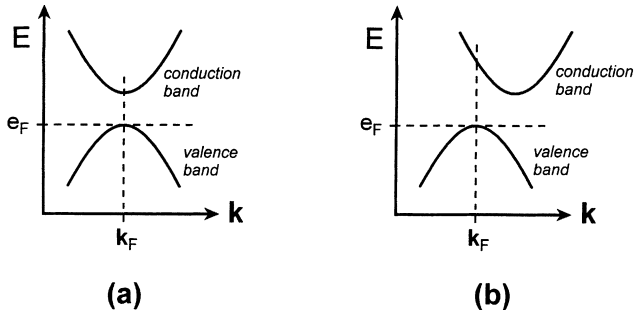


Fig. 1. Schematic representations of electronic band structures near the Fermi level for **a** a solid with a direct band gap and **b** a solid with an indirect band gap. ε_F is the Fermi level having the Fermi wave vector $\mathbf{k}_F$

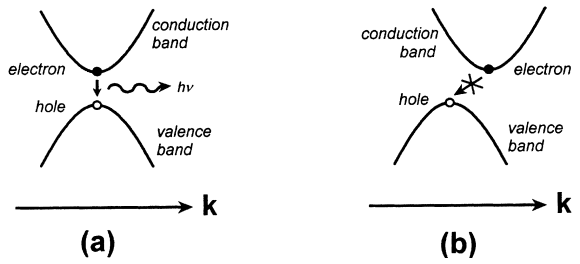


Fig. 2. Schematic representations of a radiative recombination process of free electrons and holes in **a** a solid with a direct band gap and **b** a solid with an indirect band gap. The emission is not allowed in an indirect band gap solid

with a direct band gap, light emission may be allowed. While it is necessary to consider the detailed symmetry properties of crystal orbitals to derive the actual selection rules for electronic transitions [13, 14], we focus our arguments in this paper on the presence of direct and indirect band gaps of semiconductors.

Conjugated organic polymers and organic molecular crystals have long been of interest for photoconducting and electroluminescent devices [15–22]; the relevant properties of these materials originate mostly from electrons in π-symmetry bands. Polyacetylene is the archetypal example of a conjugated organic polymer, a small band gap semiconductor which becomes highly conducting upon doping [21, 22]. The anthracene crystal, one of the most studied organic semiconducting molecular crystals, also shows intrinsic photoconductivity and electroluminescence [23, 24].

The nature of the possible conduction mechanisms has been a pressing problem in the field. It seems that a simple one-electron energy band model, namely a free-electron model, cannot properly describe the transport mechanism in those materials [24–31]. This is because the mobility of charge carriers in these materials is rather small, so the interactions of electrons with lattice vibrations and with themselves are not negligible. The low mobility is partly due to weak interactions between monomer units and randomly distributed impurities and defects. However, the band model is still useful when the interactions between monomer units are relatively strong, resulting in high mobility [32]. In fact, the electronic behavior of organic conducting and superconducting materials, where intermolecular interactions are strong, is described well with one-electron band theory [33–41]. Moreover, the electron mobility in the naphthalene crystal was reported to follow a band model in the low temperature region, where lattice vibrational motion is suppressed [42, 43].

For organic semiconductors, band structure calculations have also provided valuable information for controlling the band gap size of organic semiconductors [44–47]. Dimensionality, topology and the actual geometry of the monomer units are considered in this so-called "band gap engineering". To our knowledge, however, there has been no theoretical or experimental work directed at understanding and design of the direct or indirect nature of band gaps of organic semiconductors.

In our work, therefore, we aim to learn how we can control the band gap types, making them direct or indirect. We begin by indicating how the valence and conduction bands of one-dimensional organic solids are formed from the HOMO and the LUMO of the repeating unit, and show how the band gap type can be related to the electronic properties of the repeating unit. With the basic concepts developed in Sect. 2, a detailed analysis is carried out for organic polymers and one-dimensional sublattices of molecular crystals in the subsequent sections. The aim is to provide systematic and practical guidelines in designing a band gap type.

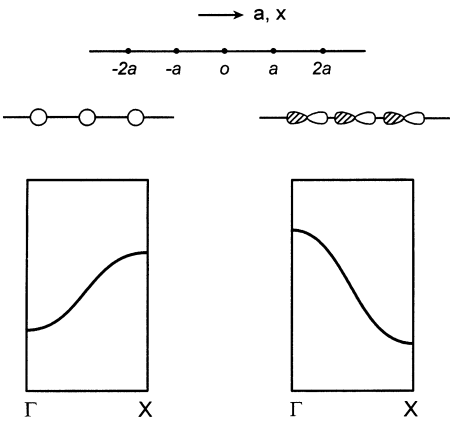
All band structures in this work were calculated by the extended-Hückel tight-binding calculation method [48, 49] implemented in the YAeHMOP program [50]. A weighted H_{ij} formula was used, as were the following atomic parameters (H_{ii} = orbital energy, ζ = Slater exponent): C 2*s*, −21.4 eV, 1.625; 2*p*, −11.4 eV, 1.625: H 1*s*, −13.6 eV, 1.3.

2 Basic concepts

One interesting feature of bands is how their energy curves (dispersion curves) "run" [51]. Within a simple Hückel approximation, the equation for the energy of a linear chain **1** having one atomic orbital in a unit cell of length *a* is

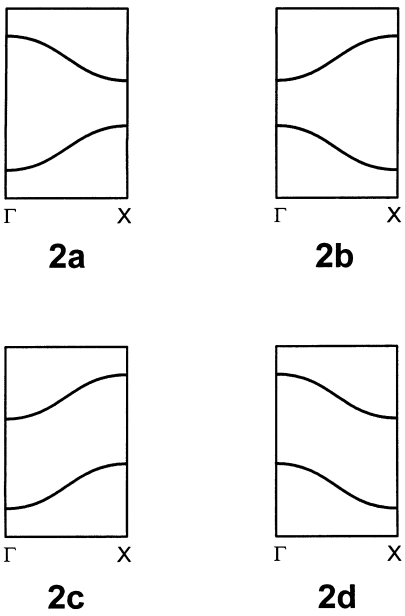
$$\varepsilon(k) = \alpha + 2\beta \cos ka \ ,$$

where α and β are the Coulomb and the nearest neighbor resonance integrals of the orbital, and k is a wave vector in the range $-\pi/a < k \leq \pi/a$. For a chain of *s* orbitals, such as a hypothetical hydrogen chain, it is expected that $\varepsilon(k = 0, \text{ at } \Gamma) < \varepsilon(k = \pi/a, \text{ at X})$, because a positive overlap between *s* orbitals results in a negative β(**1a**). However, the opposite will hold for a linear chain of p_x orbitals propagating along the *x*-axis; the basis set overlap is negative, resulting in a positive β (**1b**). Thus, the *s* band "runs up", while the p_x band "runs down" from Γ to X. In general, it is the topology of orbital interactions that determines which way bands run. (The topological aspects of orbital interactions between conjugated fragments have been stressed in the context of the stability of hydrocarbons [52]).



1a **1b**

Let us now imagine a linear chain with two atomic orbitals at each site, leading to two nonoverlapping bands. For example, we might consider a chain having s and p_x orbitals at each atomic site, without significant s-p_x mixing. Since s and p_x bands run up and down, respectively, the band structure of the chain will look like **2a**. More generally, depending on how the two bands run, four different types of band structures might occur for a chain with two non-overlapping bands, as shown in **2a–d**. When one band runs up and the other down as in **2a** or **b**, the two bands derive from orbitals with different nodal properties at each site (different topologies of interaction). In **2c** and **d** both bands run in the same way, implying that the bands originate from orbitals having the same nodal property.



2a **2b**

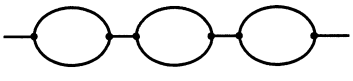
2c **2d**

Suppose there are two electrons at each site in the linear chain described above. The Fermi level will then be at the top of the lower band. It is clear that cases **2a** and **b** have a direct band gap, while **2c** and **d** have an indirect one. In general, a direct band gap will be found in the chain when the valence and conduction bands are made up of orbitals with different topologies of interactions. When the basis orbitals have the same topological properties (nodal structure) in their interaction, we expect an indirect band gap.

The same logic applies for one-dimensional organic semiconductors, and thus we can predict the band gap types of those materials, given the phase relationship of the HOMO and the LUMO of the constituent monomeric repeating unit and the connection pattern between the monomers. What we mean by this will become clear once we look at some specific examples. An assumption is implicit in this statement – there exists neither severe crossing nor mixing between the bands, especially near the Fermi level. This is always true for molecular crystals in which the orbital interactions between molecules are weak over van der Waals separations. It is also the case for most, but not all, organic polymers, as we will see.

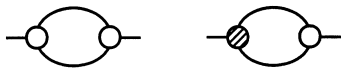
3 Conjugated polymers

Consider a planar conjugated organic polymer whose p orbitals in π bands are perpendicular to the plane. The polymer is shown schematically in **3** in which an ellipsoid represents a monomer unit. Each ellipsoid is connected to its neighbors through a simple single C—C bond, depicted by a single straight line. The heavy dots on each monomer are the atomic connection sites. In considering the phase (or "nodal" in a broader sense) relationships of the π molecular orbitals (MOs), our interest is naturally in the π MO coefficients at those connection sites. We can conveniently recognize two possible types of π MOs (**4a**, **b**) when the coefficients are nonzero. (Nonbonding MOs with zero orbital coefficients at the connection sites are not of direct interest in the context of this paper, since they give nondispersive bands. However, they are an essential ingredient for designing ferromagnetic organic polymers [53].) In **4a** and **b**, the open and lined circles represent p orbitals of positive and negative phases, respectively, projected on the sheet.[2] An MO of type **4a** should behave like the s orbital in **1a**, since the two connection sites have the same phase. To put it another way, as far as the orbital interaction pattern along the chain is concerned, situation **4a** and s orbitals are topologically similar, leading to bands that run up. On the other hand, since they have the same phase relationship of a propagating p_x orbital in **1b**, the bands generated from MOs of type **4b** should run down.



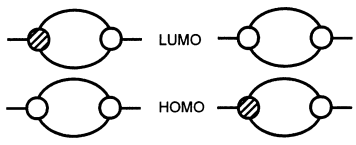
3

[2] In general, the coefficients at the connection sites need not be equal in magnitude. In most cases we discuss, they actually are

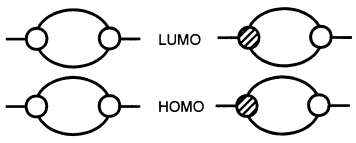


4a **4b**

For a monomer with one filled and one unfilled MO, a HOMO and a LUMO, there are four possible situations, depending on the relative phases of the connection sites. These are shown in **5a–d**. The band structures corresponding to **5a–d** will be of types **2a–d**, respectively. In essence, to predict whether a polymer has a direct or an indirect band gap, we just need to know the "nodal pseudosymmetries" of the HOMO and the LUMO of the constituent monomers at the connecting atomic sites. When the HOMO and the LUMO of the monomer have different phase relationships at the connection sites, the band gap of the corresponding polymer is expected to be direct. With the same phase relationship for the HOMO and the LUMO, the band gap should be indirect.



5a **5b**



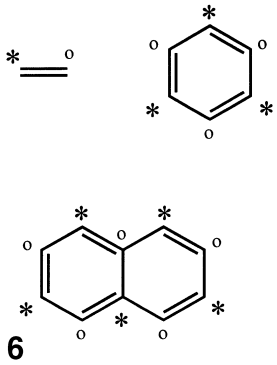
5c **5d**

The reason for our use of the pseudosymmetry description is that in lower symmetry situations, the actual coefficients at the two connection sites may not be plus or minus each other, but may differ in magnitude. Nevertheless, the phase/band gap nature relationship will still hold.

4 Even alternant hydrocarbons

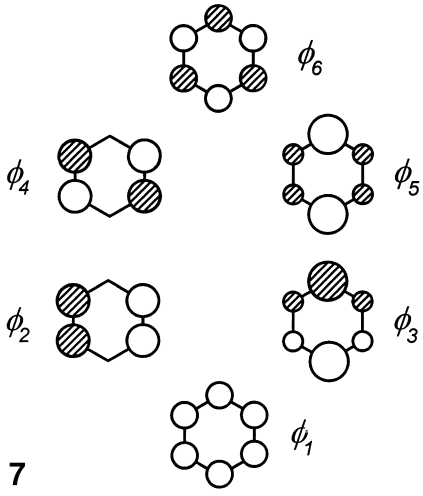
The situation becomes even simpler for the polymers constructed of a certain group of conjugated organic molecules called "even alternant hydrocarbons (even AH's)". For these molecules, we do not even need to know the shapes of the HOMO and the LUMO of the monomer to predict the band gap type, but simply the points of connection in forming the polymer.

An AH is defined as one in which it is possible to divide the carbon atoms into two sets, such that no two atoms belonging to the same set are joined by a bond [54–57]. This implies that an AH can contain no odd-membered rings. An even AH consists of an even number of carbon atoms, while an odd AH has an odd number of atoms. Traditionally the atoms of the different sets are distinguished by labeling with a star all those of one set and all those of the other set with an "o" as illustrated for some even AHs in **6**.



6

For an even AH, one of the early triumphs of Hückel theory is the "pairing theorem". This tells us that each π MO with energy $\alpha + g\beta$ (g is a real constant number) is paired with an MO with energy $\alpha - g\beta$ whose wave function differs only by a change in sign of the coefficient at each atom of one set (either $*$ or o) [54–57]. An example makes the situation clear: the π MOs of benzene come in pairs, ϕ_1 and ϕ_6, ϕ_2 and ϕ_4, and ϕ_3 and ϕ_5, and their coefficients are shown graphically in **7**.



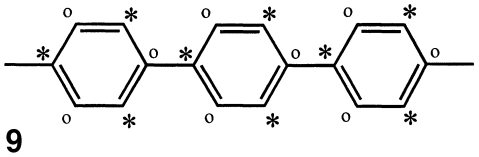
7

The pairing theorem is important for us, in that the phase relationships of the HOMO and the LUMO become available without any calculation. Thus, in an even AH with half of its levels filled, a HOMO will always be paired with a LUMO. The polymers (**3**) then fall into two different groups, depending on whether the two connection sites in each monomer belong to the same set ($*$ or o) or not, as shown in **8a** and **b**, respectively. In the case of **8a** (connection points either both starred or both unstarred), there is no phase change between the HOMO and the LUMO. Such a polymer's bands will generate pattern **5c** or **d**, i.e., band structures such as those of **2c** and **d**, or an indirect band gap. In the case of **8b** (con-

nection by one starred site, one unstarred), there is a phase change between the HOMO and the LUMO, leading to a direct band gap situation. Once overlap is included in the calculations (as it is in the extended Hückel method), the absolute values of the coefficients are no longer the same for the paired MOs [48]. However, the signs of the coefficients still follow the pairing theorem, and hence the phase relationship between the HOMO and the LUMO obtained from the simple Hückel method still holds.

8a **8b**

As an example consider poly (*p*-phenylene) **9** in which benzene molecules are connected through their para-positioned carbons. As **9** shows, this alternant polymer belongs to type **8b**, and it is anticipated that the polymer has a direct band gap. The band structure calculated with the extended Hückel method for poly (*p*-phenylene) is shown in Fig. 3. Indeed, we see a direct band gap. Examination of the crystal orbitals confirms that the valence and conduction bands come from the paired HOMO ϕ_3 and LUMO ϕ_5 in **9**, respectively. The two relatively nondispersive bands crossing valence and conduction bands are from the other HOMO-LUMO pair (ϕ_2 and ϕ_4), which have zero coefficients at the connection sites.



9

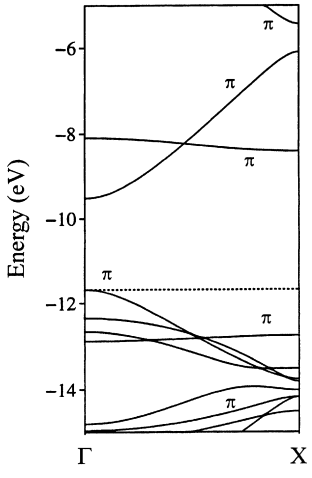
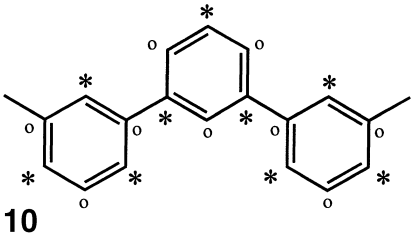


Fig. 3. Electronic band structure of poly (*p*-phenylene) **9**. A *dashed line* indicates the Fermi level, and the π bands are labelled. Carbon-carbon bond distances (1.39 Å within the ring and 1.51 Å between the rings) are chosen by averaging the values from Ref. [58]

Closely related to poly (*p*-phenylene) are poly (*p*-phenylene vinylene) (PPV) and its derivatives. Recently, much effort has been devoted to these polymers because of their promising electroluminescent properties [59–64]. PPV is made of two alternating monomer units, phenyl and vinyl groups. There is experimental evidence that the polymer's photoconductivity is consistent with a band rather than with an exciton model [62, 63]. PPV is an even AH and belongs to group **8b**, with two connection sites in a unit cell, one starred and the other unstarred. Thus, the predicted band gap is of the direct type. This is in agreement with our band structure calculation result (not shown) with the extended Hückel method as well as with band structures computed with the valence effective Hamiltonian method [64]. The direct nature of PPV's band gap conserves momentum in an optical transition process, which is essential for its efficient electroluminescence.

To form a polymer with an indirect band gap, based on benzene, one might think of connecting meta-positioned carbon atoms, belonging to the same set. However, the most likely conformation of poly (*m*-phenylene) also turns out to have a direct band gap! The reason is interesting, and shows that one must examine these systems closely. The planar poly (*m*-phenylene) structure is shown in **10**. The unit cell actually has *two* phenyl rings in it; given normal C—C—C bond angles and a planar constraint (assumed), it cannot be otherwise. It should be mentioned that it is possible to build a non-planar, helical poly (*m*-phenylene) model along the lines of the polymers discussed by Yoshizawa and Hoffmann [65], and Genin and Hoffmann [66]. We chose not to consider such helical polymers in this paper. As **10** shows, the connection points in the doubled until cell are one starred, one unstarred, implying a direct gap; Though not shown here, this is what a calculation gives.



10

By examining many polymers made of even AHs, we found that direct band gaps occur much more frequently than indirect ones. This is understandable from the nature of the sample set, in that it contains mostly six-membered rings. In these rings, the connection sites needed to make a perfectly linear chain always belong to different sets (e.g., see benzene and naphthalene molecules in **6**). A chain formed by connecting positions in the same set has to be zig-zag in shape (assuming planarity), which in turn leads to a doubled unit cell, thereby giving rise to a direct gap.

One way of avoiding these problems is to make the poly (*m*-phenylene) structure linear in some way. This can be achieved by adding an additional bond

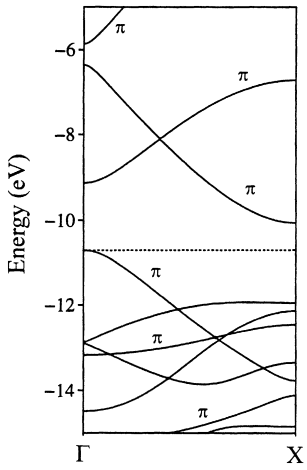
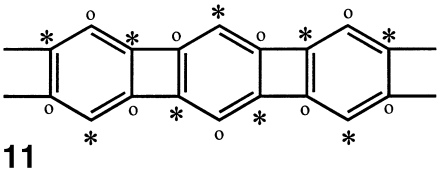


Fig. 4. Electronic band structure of **11**. A *dashed line* indicates the Fermi level, and the π bands are labelled. Carbon-carbon bond distances (1.40 Å within the six-membered ring and 1.51 Å between those rings) are chosen by averaging the values from Ref. [78]

between the monomers, as in a polyphenylene (**11**).[3] Polymers of this structural type are called "ladder polymers" [46, 67–75], and in fact, have been studied for practical applications in preparing some electroluminescent devices [76, 77]. One advantage of the ladder polymers is that their band width may be greater than that of the singly connected polymers, simply because there are more intermonomeric bonds. The result is that charge carriers can move more freely.

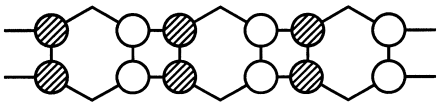


11

The calculated band structure of **11** is shown in Fig. 4; it shows an indirect band gap. The four π bands near the Fermi level derive from the MOs ϕ_2 to ϕ_5 in **7**. Due to their larger coefficients at the connection sites, the bands from ϕ_2 and ϕ_4 (i.e., ψ_2 and ψ_4) are broader than those from ϕ_3 and ϕ_5 (i.e., ψ_3 and ψ_5). The indirect nature of the band gap is in agreement with the phase relationship between ϕ_2 and ϕ_4. As expected for a doubly connected ladder polymer, the band width of the valence (3.0 eV) and conduction (3.5 eV) bands is greater than the ones of singly connected poly (*p*-phenylene) and poly (*m*-phenylene) (2.1 and 3.4 eV for poly (*p*-phenylene), and 0.5 and 0.6 eV for poly (*m*-phenylene)).

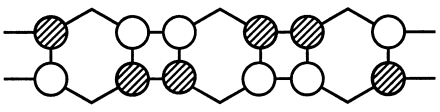
The band gap (0.6 eV) of **11** is actually quite small compared to other organic semiconductors [for example, 2.2 eV computed for poly (*p*-phenylene) and 2.9 eV for poly (*m*-phenylene)]. This can be understood by examining the crystal orbitals at the top of valence band [$\psi_2(\Gamma)$] and at the bottom of the conduction band [$\psi_4(X)$]. They are depicted in **12a** and **b**, respectively. Due to the symmetries of the original MOs, ϕ_2 and ϕ_4, nonzero orbital coefficients of those crystal orbitals occur only in the four-membered rings. These orbitals will be exactly nonbonding, if the bond distances in the four-membered ring are all the same. **11** would be then a zero-band-gap semiconductor. In reality, however, the bond distances in the four-membered ring are not the same. The bonds connecting the six-membered rings are slightly longer (~0.1 Å) than the ones within those rings [78]. This gives rise to small amounts of bonding and antibonding character in **12a** and **b**, respectively. The polymer has a small band gap – the crystal orbital at the top of valence band, **12a**, has a slightly lower energy than the one at the bottom of the conduction band, **12b**.[4] The small band gap value of **11** is important, because (combined with the broad band width) it might lead to high intrinsic conductivity solely from thermal excitation. Moreover, an indirect band gap is rare among polymers. We would like to encourage further experimental work on this system.

$\psi_2(\Gamma)$



12a

$\psi_4(X)$

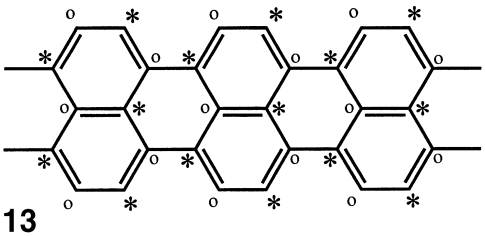


12b

A more extensively studied ladder polymer is poly (perinaphthalene) (PPN) **13**, whose monomer unit is naphthalene, an even AH. Both experiments and calculations have suggested that PPN is a small band gap semiconductor, exhibiting high intrinsic conductivity [68, 69]. The arrangement of $*$ and o in **13** indicates that PPN belongs to case **8b**, and a direct band gap is anticipated. Though not shown here, our band calculation as well as those of others [69] confirms this.

[3] One might choose a different repeating unit as the monomer, for example, a cyclobutadiene with two methylene groups attached. Whatever repeating unit we choose, however, the polymer always belongs to case **8a**, and the result does not change

[4] A smaller band gap still is calculated for polyacene. This polymer is an extreme case, showing very strong intermonomer interactions. There are two equivalent ways of defining its monomer unit, i.e., *cis*- or *trans*-butadiene. Either way, the polymer is of type **8b**, which is consistent with its direct band gap found theoretically at X. The strong intermonomer interactions do not change how the bands run, but make the shapes of the valence band crystal orbitals at X much different from those of the monomer HOMO and LUMO. For the detailed band structure analysis of polyacene, see, for example Ref [79]

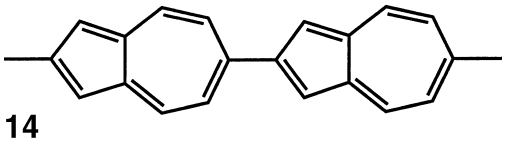


13

5 Nonalternant hydrocarbons

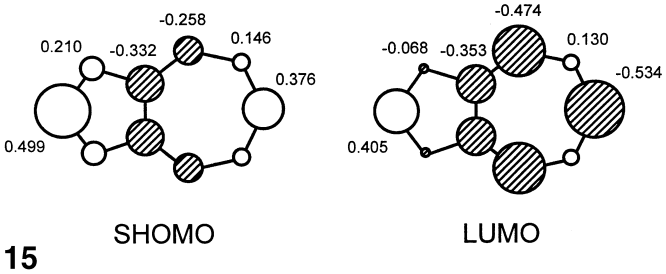
Hydrocarbons containing odd-membered rings are nonalternant. For nonalternants the pairing theorem does not hold. To predict the band gap type, therefore, we need the molecular orbitals of the constituent monomer unit. There is also a geometrical peculiarity; the odd-membered rings cannot form a perfectly linear polymer, but lead to a zig-zagged structure because the two connection sites in an odd-membered ring never "face" each other directly. Some important polymers containing five-membered rings are polypyrrole, polythiophene, and polyisothianaphthene, and their most likely conformations are all zig-zagged. Ladder formation also does not "straighten" the odd-membered ring polymers.

A hypothetical polyazulene **14** is, however, a linear polymer.[5] Linearity is achieved by connecting two carbon sites in the vertical mirror plane of azulene.



14

The HOMO of azulene (not shown here) is asymmetric with respect to the vertical mirror plane. Thus it has zero coefficients at the connection sites and will give a nondispersive band in the polymer. The second HOMO (SHOMO) lies right below the HOMO, by 0.67 eV. Its large π coefficients at the connection sites (**15**) will lead to a relatively broad band. The LUMO also has large π coefficients at the connection sites. In **15** we see that the phase relationships of the SHOMO and the LUMO are different at the connection sites. A direct band gap is expected between the SHOMO and the LUMO bands.



15

[5] Two other types of polyazulenes have been synthesized and characterized. In both cases, however, the connection sites are in the five-membered ring (and can be analyzed using similar reasoning). See Ref. [80]

The calculated band structure of **14** is shown in Fig. 5. The slopes of the bands were quite predictable. As anticipated, a direct band gap occurs between the SHOMO and the LUMO bands. The azulene HOMO is responsible for the nearly nondispersive band just below the Fermi level. The SHOMO band below is broad enough to cross the HOMO band, and hence the top of the valence band has the character of the SHOMO. Other linear polymers made up of nonalternants, for example, polypentalene, are susceptible to an analogous analysis.

6 Stacks of conjugated molecules

In contrast to the case of conjugated organic polymers, in one-dimensional stacks of conjugated molecules the orbital interactions between molecular units are between π orbitals interacting in a σ way. The arrangement of p orbitals along the stacking direction is close to that of the p_x orbital chain of **1b** [82]. To examine the consequences of this difference, consider an ethylene stack, **16**, running along the x-direction. The π HOMO of an ethylene molecule is a bonding combination of two p_x orbitals, whereas the π^* LUMO is an antibonding one. The intermolecular orbital interaction occurs (weakly) across a van der Waals gap (~3.4 Å), typical of stacking separations in this group of molecular crystals. The weak σ-type interactions of the π MOs between the ethylene molecules result in two rather narrow nonoverlapping bands along the stacking direction.

17a and **b** show the crystal orbitals at Γ and X of the valence and conduction bands, respectively. Both bands are most antibonding at Γ and most bonding at X. The expected band structure is of type **2d**, with an indirect band gap. In general, a linear stack of perfectly overlapping conjugated molecules (not just ethylenes) will behave similarly, leading to an indirect band gap.

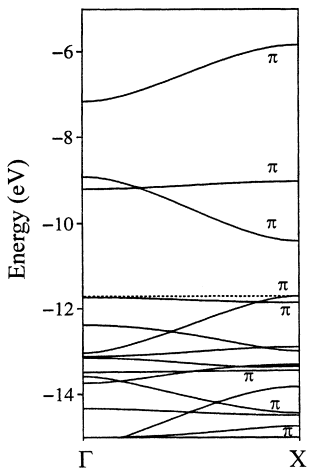
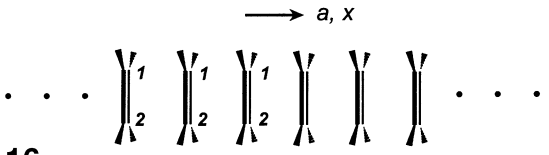
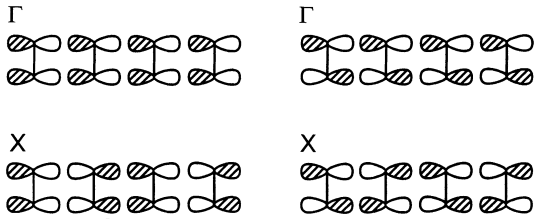


Fig. 5. Electronic band structure of polyazulene **14**. A *dashed line* indicates the Fermi level, and the π bands are labelled. Carbon-carbon bond distances in azulene are chosen from Ref. [81] assuming C_{2v} symmetry. An interazulene carbon-carbon distance of 1.5 Å is assumed

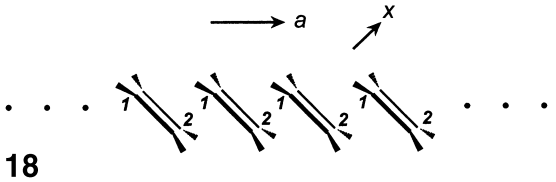


16

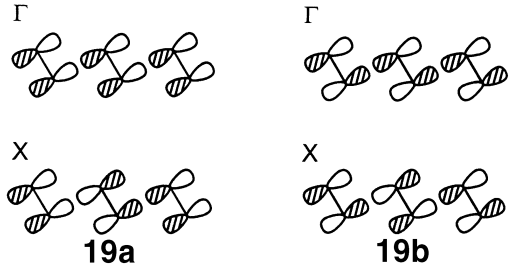


17a **17b**

One might wonder if one could ever find direct band gap materials by stacking the conjugated organic molecules. This is possible, but requires a special stacking geometry. **18** shows the ethylene molecules stacked offset, or slipped, so that the p_x orbital at carbon site 1 in one ethylene molecule interacts with the one at site 2 in the next ethylene along the stack [40]. Since the relative signs of the p_x orbitals at sites 1 and 2 are different in HOMO π versus LUMO π^*, it can be said that the phase relationships of the π MOs, as far as their interactions go, are no longer the same. The consequence of this is indicated in **19a** and **b**, in which the crystal orbitals at Γ and X are depicted for the valence and conduction bands of **18**, respectively. One may expect that the valence bands runs down, with the crystal orbitals antibonding at Γ and bonding at X. In contrast, the π^* MO of the conduction band has two lobes now of the same sign in the two interaction regions, and behaves like a chain of *s* orbitals. The conduction band should run up, bonding at Γ and antibonding at X, as shown in **19b**. The expected band structure is of type **2b**, with a direct band gap at Γ.



18

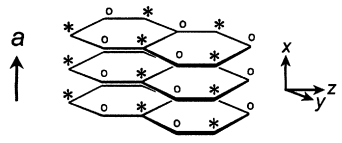


19a **19b**

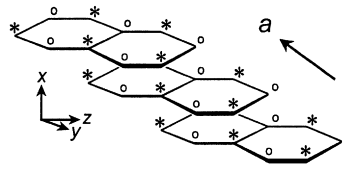
Given a conjugated molecule larger than ethylene, one can come up with many possible stackings. It is obvious that for the resultant bands to be as broad as possible, all the carbon sites need to be perfectly overlapped, as in **16**. This type of stacking always results in an indirect band gap. When the molecules are stacked askew, the potential for a direct band gap arises.

For stacks of even AHs, the pairing symmetry makes the situation quite simple; we need to know only the connectivity and topological aspect of the stacking pattern to predict the band gap types. The stacking pattern of **18** actually demonstrates the situation when a starred site in one molecule interacts with an unstarred site in the neighbor.[6]

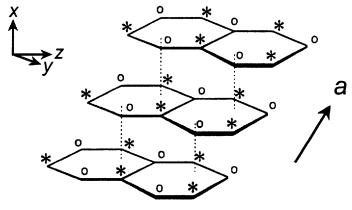
Sometimes, molecules can be stacked in such a way that the intermolecular interaction occurs only between carbon sites of the same set, say starred, although they are not perfectly overlapped but slipped. In such a case, we expect the valence and conduction bands to run parallel, giving rise to an indirect band gap. We choose stacked naphthalene molecules to illustrate this; **20a–c** show three possible ways of stacking. In **20a** and **b**, the overlapping carbon sites are in the same set, implying indirect band gaps. In **20c**, the carbon sites belonging to different sets interact, and hence a direct band gap is anticipated. Figure 6a–c corresponds to the band structures of **20a–c**, and is in agreement with our considerations. The broadest π bands occur for **20a**, due to maximized overlapping. One interesting thing we notice is that the valence and conduction bands of **20b** run up, while those of **20a** run down. This may be understood if we recall that the HOMO and the LUMO of naphthalene have a nodal plane in the middle of the molecule, perpendicular to the *y*-direction in **20a–c** [55].



20a



20b



20c

Experimentally, it has been found that photoconductivity can be strongly dependent on the stacking ar-

[6] In the ethylene molecule, an even AH, ∗ is assigned to site 1 and o to site 2

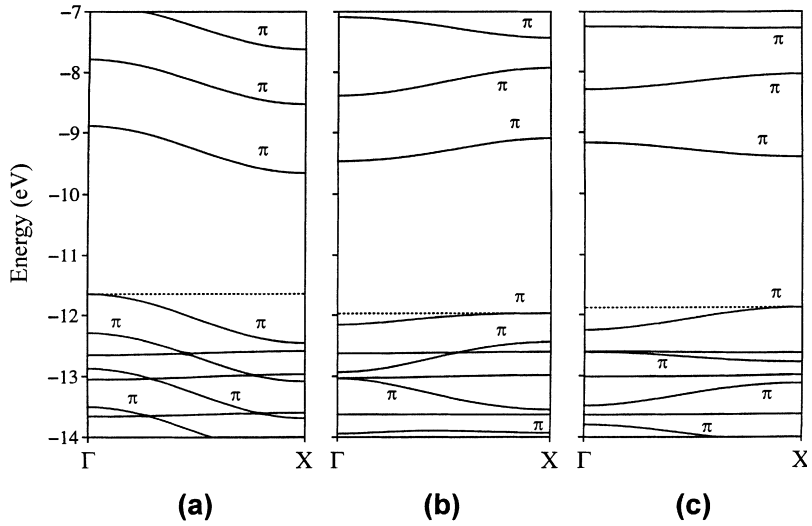


Fig. 6. Electronic band structure of naphthalene stacks with stacking patterns **a 20a**, **b 20b**, and **c 20c**. *Dashed lines* indicate the Fermi levels, and the π bands are labelled. The carbon-carbon bond distance (1.39 Å) is chosen by averaging the values from Ref. [83]

rangements for molecular crystals such as a vanadyl phthalocyanine and squaraines [17, 84]. The squaraines, especially, show higher dark decay when they are stacked askew, implying faster recombination processes, than when they are perfectly overlapped in the stack. However, due to possible (extrinsic) impurities in these crystals, it is not clear if the intrinsic electronic effect has been measured. Further experiments on suitable crystals are needed.

7 Conculsion

In designing conjugated but semiconducting polymers or molecular crystals, it is often assumed that the inherent physical and chemical properties of monomer units will be preserved in the extended materials. If the interaction between monomer units is relatively weak, this is certainly justified. The band gap that results may be classified as direct or indirect. Which type of band gap the material has is important, because the likelihood of optical absorption or emission of the solid near the band gap energy is directly dependent on its band gap type.

The band gap type, be it direct or indirect, is characteristic of extended systems, not of molecules. There is no analogous property in molecular systems. We have shown how the band gap type is determined by the characteristics of the constituent molecules. In essence, the phase relationships of the coefficients of the HOMO and the LUMO of monomers in the interaction regions determine how the valence and conduction bands run in reciprocal space. When the HOMO and the LUMO have topologically similar phase relationships in the interaction regions, an indirect band gap will occur. Otherwise, the system will possess a direct band gap. The pairing symmetry of even AHs makes this class of molecules particularly easy to analyze. Only the polymer connectivity information or the stacking pattern is required to determine the band gap type of even AHs.

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