



## HIGHER ORDER PEIERLS DISTORTION OF ONE-DIMENSIONAL CARBON SKELETONS

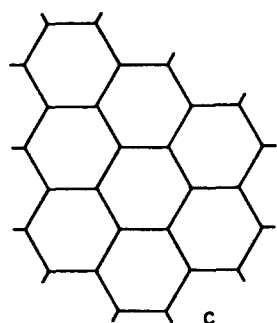
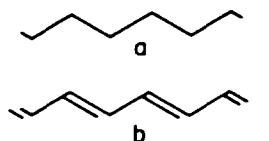
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In some one-dimensional chains with metallic band structures the energetically most advantageous distortion opens an energy gap non-linear in the distortion. The absence of a linear Peierls effect is due to the symmetry of the degenerate pair of orbitals at the Fermi level: they do not interact directly in the distorted system. The effect provides a natural bridging of the one-dimensional polyacetylene (linearly Peierls-distorted) to the two-dimensional graphite (not distorted) carbon skeletons. The simple explanation bears some generality.

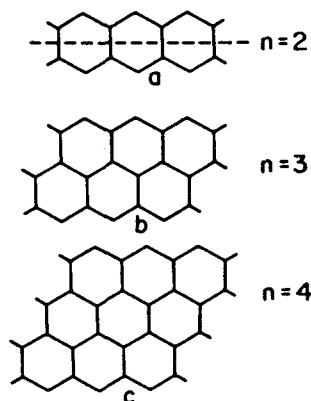
Polyacetylene ((CH)<sub>x</sub>, polyene, 1a, b)  
has a Peierls-distorted<sup>1</sup> ground state. This



(I)

chain of sp<sup>2</sup> carbon atoms with each C contributing one delocalized 2p<sub>z</sub> or π orbital and electron, has alternating short and long

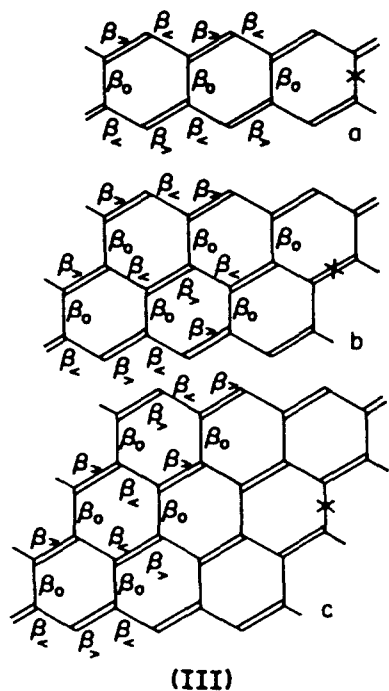
C-C bonds.<sup>2,3</sup> On the other hand, the structural essence of graphite, the two-dimensional sp<sup>2</sup> carbon layer has equivalent C-C bonds (1c). It is legitimate to ask how a series of system of intermediate complexity would behave with respect to bond alteration, i.e. how the passage from (CH)<sub>x</sub> to a graphite layer is accomplished. One member of such a series, polyacene (IIa) has been recently studied by Kivelson and Chap-



(II)

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man and Yamabe *et al*<sup>4</sup>. The latter concluded that polyacene should have a metallic band structure and that it should not undergo a Peierls distortion. This is in contrast with a previous calculation<sup>5</sup> where the band structure of the alternating system (IIIa) has an en-



ergy band gap and is more stable than the regular structure (IIa).

In this work we examine the  $\pi$ -electron band structure of polyacene, and two further members of the series (IIb,c) as well as their tendency to distort. We conclude that while all these chains do distort into a structure with lower symmetry (III) the energy gap openings decrease sharply with the number of coupled polyenic chains ( $n$ ) according to a power law  $E_g = C_n (\delta/\beta_0)^n$ , where  $|\delta/\beta_0| < 1$ . (The  $\beta_0$  hopping integral is negative).

### Polyacene

Figure 1 reproduces the essential part of the band structure published previously

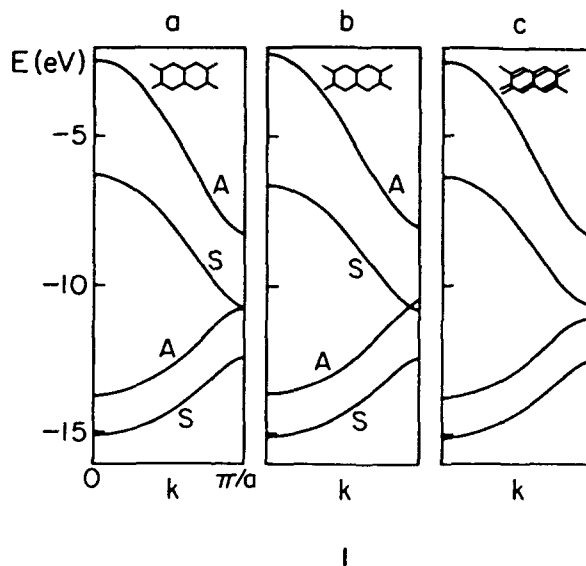
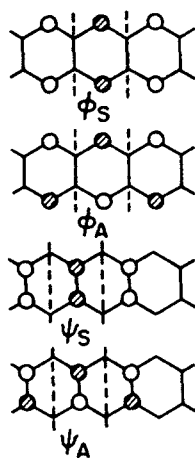


Figure 1. Band structures of polyacene. (a) Regular with second neighbor interaction<sup>3,4</sup> (IIa) (b) Regular with long-range neighbor interactions<sup>5</sup>. (c) Distorted according to (IIIa).

for polyacene<sup>5</sup>. The bands with  $\pi$  symmetry, which are the only relevant ones for this discussion are depicted. Symmetry labeling corresponds to reflections along the dotted lines in (IIa). The previously published band structure calculations differed, among other things, by the extent of the lattice summations. These were carried out in Reference 4a by restricting them to second nearest neighboring atoms, in contrast to the rather converged lattice sums of Reference 5.

The present discussion is based on second neighbor lattice sums, because in the

particular systems studied here this restriction enables us to fully decouple the  $\pi$  orbitals of the outermost (edge) carbon atoms from the rest at  $k = \pi/a$ , as can be seen in (IV) for polyacene. This idealisation in-



(IV)

creases the symmetry of the system. In particular, the decoupling is a consequence of the transverse mirror planes also shown in (IV), permitting a consistent interpretation of the previously published band structures. Due to this decoupling described above,  $\psi_S$  and  $\psi_A$  are degenerate at  $k = \pi/a$ , as obtained before<sup>3,4a</sup> (Figure 1a). Third (and higher) neighbor interactions lift this degeneracy, by stabilizing  $\psi_S$  and destabilizing  $\psi_A$ , leading to the crossing in the converged calculation<sup>5</sup> (Figure 1b).

The effect of the distortion from the regular (IIa) to the alternating structure (IIIa) is to introduce a mixing of  $\psi_S$  and  $\psi_A$  as well as  $\phi_a$  and  $\phi_b$ . This is because the

transverse mirror planes vanish the moment the slightest distortion takes place<sup>6</sup>. However, the  $C_2$  axes, indicated by crosses on (III), still remain a valid symmetry operation. They prohibit the mixing of the A and S states. This new mixing at  $k = \pi/a$ , absent for the regular structure, stabilizes the highest occupied band states

$$\psi_V = \psi_a + C \phi_a \quad (1)$$

and destabilizes the lowest empty band states

$$\psi_C = \psi_S - C \phi_S \quad (2)$$

leading to a forbidden energy gap,  $E_g$  as in Figure 1c. Suppose, that  $\beta_{<} = \beta_0 + \delta$  and  $\beta_{>} = \beta_0 - \delta$  (as indicated in (IIIa)). The problem can be solved analytically, giving

$$E_g^{(n=2)} = \beta_0 + \sqrt{\beta_0^2 + 4\delta^2} \approx 2\delta^2/\beta_0 \quad (3)$$

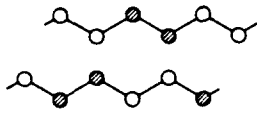
where an expansion in terms of small  $\delta/\beta_0$  has been performed. A perturbation calculation yields zero correction at first order, and the same as in (3) at second order in energy. In case of polyacetylene the gap opening is proportional to the first power of the distortion.

$$E_g^{(n=1)} = 4\delta \quad (4)$$

This is due to the direct coupling of the degenerate states of  $k = \pi/a$  as illustrated in (V). The position of  $\phi_a$  is stabilized and  $\phi_b$  is destabilized by the same amount.

#### Between Polyacene and Graphite

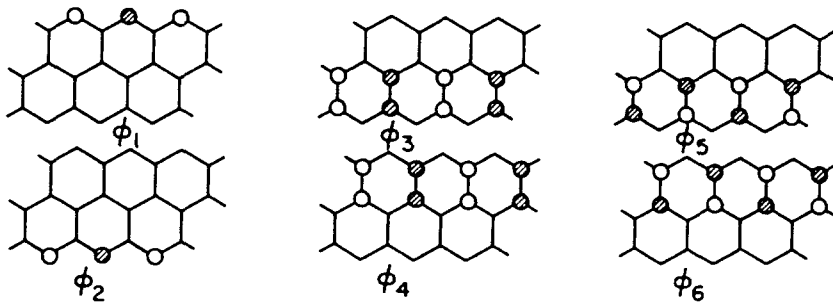
The one-dimensional polymers (IIb) (polyaphthene, let us call it poly-C<sub>6</sub>) and (IIc) (Polypyrene, let us call it poly-C<sub>8</sub>)



(V)

are members of a series that makes an obvious transition to two dimensions.

The symmetry adapted wavefunctions of  $k = \pi/a$  poly  $C_6$  are illustrated in (VI). The follow-



(VI)

ing crystal orbitals are obviously degenerate pairs ( $\varphi_1, \varphi_2$ ); and ( $\varphi_3, \varphi_4$ ); and ( $\varphi_5, \varphi_6$ ).  $\varphi_1$  and  $\varphi_2$  lie at the Fermi level. The distortion from the regular to the distorted (IIIb) structure introduces a coupling between the edge atoms of  $\varphi_1$  and  $\varphi_2$ , giving rise to a splitting as for polyacene. The lack of mixing of  $\varphi_1$  orbitals of the same symmetry is due to the restriction of the second neighbor approximation model.  $\varphi_1$  is decoupled from  $\varphi_4$  and  $\varphi_6$  because of this, while it does not interact with  $\varphi_2, \varphi_3$ , and  $\varphi_5$  due to the vertical mirror planes and the changes of signs that arise as a consequence of being at  $k = \pi/a$ . The distortion lifts some of these uncouplings. The new symmetry adapted wavefunctions will

be  $\Psi_1 (\sqrt{2}\Psi_{1,2} = \varphi_1 \pm \varphi_2, \sqrt{2}\Psi_{3,4} = \varphi_3 \pm \varphi_4,$  and  $\sqrt{2}\Psi_{5,6} = \varphi_5 \pm \varphi_6)$ . These are still degenerate for the undistorted system. In the distorted system  $\Psi_1$  interacts with  $\Psi_3$  and  $\Psi_5$ , leading to a stabilization of it by  $E_g/2$ , while  $\Psi_2$  rises by the same amount due to mixing with  $\Psi_4$  and  $\Psi_6$ . The Hamiltonian for the distorted system at  $k = \pi/a$  in terms

of atomic orbital coefficients is

$$H = \begin{pmatrix} 0 & \delta & & & & \\ \delta & 0 & 1 & & & \\ & 1 & 0 & \delta & & \\ & & \delta & 0 & 1 & \\ & & & 1 & 0 & \delta \\ & & & & \delta & 0 \end{pmatrix} \quad (5)$$

A perturbation calculation for small  $\delta$  yields

$$\Psi_1' = \Psi_1 + a\Psi_3 + b\Psi_5 \quad a = -b = -\delta/\beta_0 \sqrt{2} \quad (6)$$

therefore, even at second order in energy a

cancellation occurs. The first non-zero term for  $E_g^{(n=3)}$  is third order in energy:

$$E_g^{(n=3)} = 4\delta^3/\beta_0^2 \quad (7)$$

in a similar way for poly- $C_8$  it can be shown that

$$E_g^{(n=4)} = \text{const. } \delta^4 \quad (8)$$

### Conclusions

We have demonstrated that the first order Peierls gap opening is absent in carbon chains with 2 or more coupled polyenic chains, due to the idealized symmetry of the system. However, a higher order gap always occurs:

$$E_g^{(n)} = C_n (\delta/\beta_0)^n \beta_0 \quad (9)$$

driving the lattice to distort<sup>7</sup>.  $\delta/\beta_0$  can be realistically estimated to be about 0.2 or less. ( $\delta/\beta_0 = 0.135$  for a distortion of  $0.08 \text{ \AA}$ , a value close to the experimentally observed one for polyacetylene<sup>2</sup>). Thus, the higher order gaps will be much smaller than those of polyacetylene, where the gap is about  $1.4 \text{ eV}$ <sup>8</sup>).

As a consequence even small interchain effects may actually stabilize a metallic state in such systems<sup>4a</sup> in sharp contrast to the linear Peierls system of polyacetylene. This ac-

tually happens in graphite, which has  $E_g = 0$  and a regular structure, and not any distorted one.

We think that the above simple considerations qualify Peierls' theorem on the intrinsic instability of one-dimensional metallic systems, and have broader applicability. The higher order Peierls distortions described here may occur in other systems as well, where chains susceptible to first order Peierls distortion are strongly coupled together, forming more complicated quasi-one-dimensional semi-metallic systems.

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7. Elastic forces of the  $\sigma$ -skeleton determine the actual magnitude of this distortion, which we expect will sharply diminish as  $n$  increases. Further calculations would be needed to pin

down the crossover, which we anticipate to occur around  $n = 3$ .

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