

## Bond alternation and band structure in infinite polyacenacene

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

1990 J. Phys.: Condens. Matter 2 10003

(<http://iopscience.iop.org/0953-8984/2/50/004>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 171.66.16.151

The article was downloaded on 11/05/2010 at 07:02

Please note that [terms and conditions apply](#).

## Bond alternation and band structure in infinite polyacenacene

Chengzheng Hu

Physics Department, Wuhan University, People's Republic of China

Received 15 March 1990, in final form 25 July 1990

**Abstract.** Infinite polyacenacene has been studied by the same method as applied by Salem and Longuet-Higgins to infinite polyacetylene and polyacene. Polyacenacene can be considered as three polyacetylene chains joined by cross links. It is predicted that the most stable configuration is the equilibrium configuration exhibiting glide plane symmetry, in which the C—C bonds of three chains all have the same length, being slightly shorter than the cross bonds. This stable configuration of equilibrium has zero gap and zero slope at the Fermi level.

### 1. Introduction

In 1964, Little [1] proposed that there may exist certain organic polymers which can become superconducting at or above room temperature. This conjecture attracted great interest initially because of its importance. Little's model consists of a long molecule (spine) with side groups playing the role of polarizers. In his original proposal, polyacetylene was used as the spine of a one-dimensional superconductor. In spite of many efforts, however, such a favourable material has not been synthesized yet, and the realization of this idea encountered a series of objections [2]. One of them concerns the instability of a one-dimensional metal (Peierls [3] distortion). It is well known that for polyacetylene the regular chain is unstable with respect to Peierls distortion, leading to bond-length alternation and an opening non-zero energy gap [4]. On the other hand, the structural essence of graphite has an equivalent C—C bond with a zero band gap. Therefore it is without doubt of interest to investigate the structures and properties of a series of systems from long polyacenic molecules to a graphite layer.

One of the simplest members of such a series is polyacene, which can be considered as two polyacetylene chains joined by cross links. This polymer has not been synthesized yet. However, theoretical studies of its electronic structure have been made by a number of workers [5–9]. Some of these have pointed out that, in polyacene, Peierls distortion scarcely happens. The next member of such a series is polyacenacene, which can be considered as three polyacetylene chains joined by cross links. Only a few researchers have studied this polymer [10]. Although complete synthesis of this polymer has not yet been achieved, a highly conductive organic material, which seems to be found with condensed aromatic rings, has been prepared recently [11]. Since the atomic C-to-H ratio for this material is 3, we can consider polyacenacene as a model for this polymer.

In this paper we wish to study the bond alternation and band structure in infinite polyacene by the same method as that applied to infinite polyacetylene and polyacene [4, 5]. We use the simple molecular orbital theory neglecting atomic orbital overlap and including  $\sigma$ -bond compression. Here, using the relationship already assumed in [4, 5] between the length of a bond, its resonance integral and its mobile order in equilibrium, we show that in infinite polyacene no Peierls distortion is expected, and the most stable configuration is one in which all the C—C bonds of three chains are of length 1.413 Å and the cross bonds of length 1.433 Å. In section 2 we determine the expression for the energy of the  $\pi$  electrons in infinite polyacene. The equilibrium configuration and its stability are investigated in section 3. The  $\pi$  band structure of the stable configuration is given in section 4.

## 2. Expression for the binding energy

We would like to limit the brief description of the simple molecular orbital method, similar to that in [4, 5], to a minimum necessary for the calculation. The total energy can be expressed as the sum of a part  $E_\sigma$  due to the  $\sigma$  electrons and a part  $E_\pi$  due to the  $\pi$  electrons:

$$E = E_\sigma + E_\pi \quad E_\sigma = \sum_j f(r_j) \quad (1)$$

To calculate  $E_\pi$ , we consider a probable geometry, in which the bonds of three chains are alternately of length  $r_1$  and  $r_2$  ( $r_1 \geq r_2$ ), and the cross bonds are all of length  $r_3$  (figure 1). The corresponding resonance integrals are  $\beta_1, \beta_2$  and  $\beta_3$ , respectively ( $\beta_2 \leq \beta_1 < 0$ ,  $\beta_3 < 0$ ). The periodic forms are dictated by the translational symmetry. The boundary conditions [12] imply that the phase angle  $\theta_j$  must be a multiple of  $2\pi/N$ :

$$\theta_j = 2\pi j/N \quad (2)$$

where  $N$  is the number of unit cells. For infinite polyacene,  $N \rightarrow \infty$ .  $\theta_j$  becomes a continuous variable in the interval.  $\theta_j \rightarrow \theta$  and  $0 \leq \theta \leq 2\pi$ . The secular equation for the orbital energy  $\varepsilon$  in this configuration leads to the following form:

$$\varepsilon^6 - (3|\delta|^2 + 2\beta_3)\varepsilon^4 + (3|\delta|^4 + 2|\delta|^2\beta_3^2 + \beta_3^4)\varepsilon^2 - |\delta|^6 = 0 \quad (3)$$

where

$$|\delta|^2 = \beta_1^2 + \beta_2^2 + 2\beta_1\beta_2 \cos \theta. \quad (4)$$

It is a cubic equation in  $\varepsilon^2$ . The solutions are given, in order, by

$$\begin{aligned} \varepsilon_1 &= - \left[ \frac{2}{3}q \cos(\alpha/3) + (3|\delta|^2 + 2\beta_3^2)/3 \right]^{1/2} \\ \varepsilon_2 &= - \left\{ \frac{2}{3}q \cos[(\alpha - 2\pi)/3] + (3|\delta|^2 + 2\beta_3^2)/3 \right\}^{1/2} \\ \varepsilon_3 &= - \left\{ \frac{2}{3}q \cos[(\alpha + 2\pi)/3] + (3|\delta|^2 + 2\beta_3^2)/3 \right\}^{1/2} \\ \varepsilon_4 &= - \varepsilon_3 \quad \varepsilon_5 = - \varepsilon_2 \quad \varepsilon_6 = - \varepsilon_1 \end{aligned} \quad (5)$$

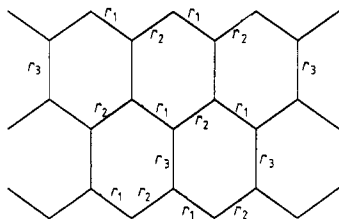
where

$$q = (6|\delta|^2\beta_3^2 + \beta_3^4)^{1/2} \quad (6)$$

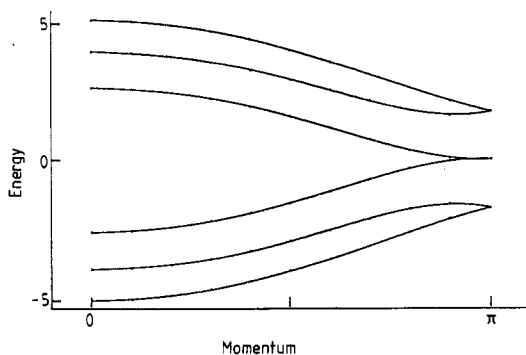
and  $\alpha$  is related to the resonance integrals by

$$\cos \alpha = [(9|\delta|^2 - 2\beta_3^2)\beta_3^4]/2q^3. \quad (7)$$

Generally, the orbitals fall into six bands. In the ground state the lowest three bands



**Figure 1.** A probable configuration of polyacenacene.



**Figure 2.**  $\pi$ -band structure of the stable configuration.

are full, each orbital containing two electrons, and the other three bands are empty. The total energy of all the  $\pi$  electrons is therefore

$$\begin{aligned}
 E_{\pi} &= -\frac{2}{\sqrt{3}} \sum_{j=1}^N \sum_{i=0, \pm 1} \left[ 3|\delta|^2 + 2\beta_3^2 - 2\beta_3(6|\delta|^2 + \beta_3^2)^{1/2} \cos\left(\frac{\alpha + 2\pi i}{3}\right) \right]^{1/2} \\
 &= -\frac{2}{\sqrt{3}} \sum_{j=1}^N \sum_{i=0, \pm 1} \left[ 3 \left[ \beta_1^2 + \beta_2^2 + 2\beta_1\beta_2 \cos\left(\frac{2\pi j}{N}\right) \right] + 2\beta_3^2 \right. \\
 &\quad \left. - 2\beta_3 \left\{ 6 \left[ \beta_1^2 + \beta_2^2 + 2\beta_1\beta_2 \cos\left(\frac{2\pi j}{N}\right) \right] + \beta_3^2 \right\}^{1/2} \cos\left(\frac{\alpha + 2\pi i}{3}\right) \right]^{1/2}. \quad (8)
 \end{aligned}$$

For infinite polyacenacene we can replace the sum by an integral, namely

$$\begin{aligned}
 E_{\pi} &= -\frac{N}{\sqrt{3}\pi} \sum_{i=0, \pm 1} \int_0^{2\pi} \left[ 3(\beta_1^2 + \beta_2^2 + 2\beta_1\beta_2 \cos \theta) + 2\beta_3^2 \right. \\
 &\quad \left. - 2\beta_3 [6(\beta_1^2 + \beta_2^2 + 2\beta_1\beta_2 \cos \theta) + \beta_3^2]^{1/2} \cos\left(\frac{\alpha + 2\pi i}{3}\right) \right]^{1/2} d\theta. \quad (9)
 \end{aligned}$$

### 3. 'Symmetrical' equilibrium configuration and its stability

We now consider an arbitrary 'symmetrical' configuration with  $r_1 = r_2$  (strictly speaking, the symmetry is glide plane symmetry). We want to calculate the equilibrium bond length and to know whether the symmetrical equilibrium configuration is stable or unstable as the bonds of three chains are alternately increased and decreased slightly in length.

To determine the values of  $r_1$  and  $r_3$ , which give a symmetrical configuration of static equilibrium, we need an expression for the mobile orders  $p_1$  and  $p_3$  of the bonds in terms of  $\beta_1$  and  $\beta_3$ . By definition, it is easy to see that

$$\begin{aligned} p_1 &= (1/6N) \partial E_\pi / \partial \beta_1 \\ p_3 &= (1/4N) \partial E_\pi / \partial \beta_3 \end{aligned} \quad (10)$$

for polyacene. From equation (9) we find that

$$\begin{aligned} p_1 = p_2 &= \sum_{i=0, \pm 1} \int_0^{2\pi} I_1(i, \lambda, \theta) d\theta = \frac{1}{12\sqrt{3}\pi} \sum_{i=0, \pm 1} \\ &\times \int_0^{2\pi} \frac{\{6\lambda(1 + \cos \theta) + 12\lambda(1 + \cos \theta) \cos[(\alpha + 2\pi i)/3]/u + 2uf_1(i)\}}{S(i)} d\theta \\ p_3 &= \sum_{i=0, \pm 1} \int_0^{2\pi} I_3(i, \lambda, \theta) d\theta = \frac{1}{4\sqrt{3}\pi} \sum_{i=0, \pm 1} \\ &\times \int_0^{2\pi} \frac{\{2 + 2[1 + 6\lambda^2(1 + \cos \theta)] \cos[(\alpha + 2\pi i)/3]/u + uf_3(i)\}}{S(i)} d\theta \end{aligned} \quad (11)$$

where

$$u = 1 + 12\lambda^2(1 + \cos \theta) \quad \lambda = \beta_1/\beta_3$$

$$\begin{aligned} f_1(i) &= \beta_3 \frac{\partial \cos[(\alpha + 2\pi i)/3]}{\partial \beta_1} \\ &= \{9\lambda(1 + \cos \theta)[1 - 2\lambda^2(1 + \cos \theta)] \sin[(\alpha + 2\pi i)/3]\}/W \end{aligned}$$

$$\begin{aligned} f_3(i) &= \beta_3 \frac{\partial \cos[(\alpha + 2\pi i)/3]}{\partial \beta_3} \\ &= -\{18\lambda^2(1 + \cos \theta)[1 - 2\lambda^2(1 + \cos \theta)] \sin[(\alpha + 2\pi i)/3]\}/W \end{aligned}$$

$$S(i) = \{6\lambda^2(1 + \cos \theta) + 2 + 2u \cos[(\alpha + 2\pi i)/3]\}^{1/2} \quad (i = 0, \pm 1)$$

and

$$W = [1 + 12\lambda^2(1 + \cos \theta)]\{[1 + 12\lambda^2(1 + \cos \theta)]^3 - [1 - 9\lambda^2(1 + \cos \theta)]^2\}^{1/2}. \quad (12)$$

It can be proved that the integrals in equation (11) are convergent.

Following [4, 5], the length of a bond in equilibrium is assumed to be related to its mobile order by the approximate formula

$$r_i (\text{\AA}) = 1.50 - 0.15 p_i \quad (13)$$

established empirically for  $C(sp^2)-C(sp^2)$  bonds, and the dependence of the resonance integral of a bond on its length is assumed to take the exponential form

$$\beta_i = -B \exp(-r_i/a) \quad (14)$$

where the exponent  $a$  has the value  $0.3106 \text{\AA}$ . Thus using equations (13) and (14) we get

$$p_1 - p_3 = (0.3106/0.15) \ln \lambda. \quad (15)$$

On the other hand, from equation (11)

$$p_1 - p_3 = \sum_{i=0, \pm 1} \int_0^{2\pi} [I_1(i, \lambda, \theta) - I_3(i, \lambda, \theta)] d\theta. \quad (16)$$

Plotting  $p_1 - p_3$  against  $\lambda = \beta_1/\beta_3$  in accordance with equations (15) and (16), we obtain

two curves. The intersection occurs at  $\lambda = 1.066$ . The corresponding mobile bond order calculated from equation (11) are

$$p_1 = p_2 = 0.5789 \quad p_3 = 0.4446. \quad (17)$$

Substitution of these values into equation (13) gives the equilibrium bond lengths as

$$r_1 = r_2 = 1.4132 \text{ \AA} \quad r_3 = 1.4333 \text{ \AA}. \quad (18)$$

We are now in a position to investigate the stability of the symmetrical equilibrium configuration just found when the bond lengths of three chains are alternatively increased and decreased slightly. Suppose that a distortion can be represented by keeping  $\beta_3 = -B \exp(-r_3/a)$  constant and writing

$$\beta_1 = \beta_0 \exp(-x) \quad \beta_2 = \beta_0 \exp(x) \quad (19)$$

where

$$\begin{aligned} \beta_0 &= -B \exp(-r_1/a) = -B \exp(-r_2/a) \\ \Delta r &= \pm ax. \end{aligned} \quad (20)$$

$r_1$ ,  $r_2$  and  $r_3$  have the values given by equation (18).  $\Delta r$  is the change in bond length in three chains. For any configuration of static equilibrium the condition

$$(\partial E/\partial x)_0 = (\partial E_\sigma/\partial x)_0 + (\partial E_\pi/\partial x)_0 = 0 \quad (21)$$

must hold, namely [4]

$$df/dr + 2p d\beta/dr = 0. \quad (22)$$

From equations (13) and (14) it follows that

$$df/dr = (2\beta/a)(1.50 - r)/0.15. \quad (23)$$

To study the stability of the symmetrical equilibrium configuration, we need the second derivative of  $E$  with respect to  $x$ :

$$(\partial^2 E/\partial x^2)_0 = (\partial^2 E_\sigma/\partial x^2)_0 + (\partial^2 E_\pi/\partial x^2)_0. \quad (24)$$

With the aid of equations (1) and (23),  $(\partial^2 E_\sigma/\partial x^2)_0$  can be expressed as

$$(\partial^2 E_\sigma/\partial x^2)_0 = 6Na^2(d^2f/dr^2)_{r=r_1=r_2} = -12N\beta_0(a/0.15 + p_0). \quad (25)$$

Using equations (9) and (19), we find that

$$\begin{aligned} (\partial^2 E_\pi/\partial x^2)_0 &= \frac{2N}{\sqrt{3}\pi} \beta_0 \sum_{i=0,\pm 1} \int_0^{2\pi} K(i, \lambda, \theta) d\theta \\ &= \frac{2N}{\sqrt{3}\pi} \beta_0 \sum_{i=0,\pm 1} \int_0^{2\pi} \frac{6\lambda^2 + 12\lambda^2 \cos[(\alpha + 2\pi i)/3]/u + uG(i)}{\lambda S(i)} d\theta \end{aligned} \quad (26)$$

where

$$\begin{aligned} G(i) &= (\partial\{\cos(\alpha + 2\pi i)/3\}/\partial x)/\sinh(2x)_0 \\ &= \{6\lambda[1 - 2\lambda^2(1 + \cos \theta)] \sin[(\alpha + 2\pi i)/3]\}/Q \quad (i = 0, \pm 1) \end{aligned} \quad (27)$$

and

$$Q = u^2[6(1 + \cos \theta) + 39\lambda^2(1 + \cos \theta)^2 + 192\lambda^4(1 + \cos \theta)^3]^{1/2}. \quad (28)$$

$u$  and  $S(i)$  are given by equation (12). Similarly, these integrals are all convergent. Therefore

$$\left(\frac{\partial^2 E}{\partial x^2}\right)_0 = -12N\beta_0 \left[ \frac{a}{0.15} + p_0 - \frac{1}{6\sqrt{3}\pi} \sum_{i=0,\pm 1} \int_0^{2\pi} K(i, \lambda, \theta) d\theta \right] \quad (29)$$

where  $p_0$  and  $\lambda$  have the values already calculated:  $p_0 = 0.5789$  and  $\lambda = \beta_1/\beta_3 = 1.066$ . It follows that

$$\frac{1}{6\sqrt{3}\pi} \sum_{i=0,\pm 1} \int_0^{2\pi} K(i, \lambda, \theta) d\theta = 1.4878. \quad (30)$$

Thus, remembering that  $\beta_0 < 0$ , we find that

$$(\partial^2 E/\partial x^2)_0 > 0. \quad (31)$$

It turns out that the equilibrium configuration exhibiting glide plane symmetry is one of stable equilibrium.

#### 4. $\pi$ -band structure

Figure 2 shows the  $\pi$ -band structure, corresponding to the equilibrium configuration exhibiting glide plane symmetry. One can see that all the  $\pi$  bands at the Brillouin zone boundary are doubly degenerate. In the case of polyacenacene such a double degeneracy always occurs because of its glide plane symmetry [13]. Additionally, the highest occupied (HO) and lowest unoccupied (LU) bands have zero slope at the Fermi level. In fact, from equation (5) the energy bands can be written as

$$\varepsilon(\theta) = \pm (\beta_3/\sqrt{3})\{6\lambda^2(1 + \cos \theta) + 2 + 2[1 + 12\lambda^2(1 + \cos \theta)]^{1/2} \cos[(\alpha + 2\pi)/3]\} \quad (32)$$

where  $+$  and  $-$  correspond to the HO and LU bands, respectively. It follows that

$$\begin{aligned} \partial \varepsilon(\theta)/\partial \theta &= \pm (\beta_3/\sqrt{3})(-\sin \theta)(3\lambda^2 + 6\lambda^2 \cos[(\alpha + 2\pi)/3])u \\ &+ \llbracket u \partial \{\cos[(\alpha + 2\pi)/3]/\partial \theta\} \rrbracket / (-\sin \theta) / [6\lambda^2(1 + \cos \theta) + 2 \\ &+ 2u \cos[(\alpha + 2\pi)/3]]^{1/2} \sim \mp (\sqrt{3}\lambda^2\beta_3/\sin \theta) \\ &\times [48\lambda^2(1 + \cos \theta)][1 + \dots] / [1 - (21/4)\lambda^2(1 + \cos \theta) + \dots] \rightarrow 0 \end{aligned} \quad (33)$$

when  $\theta \rightarrow \pi$  (Fermi level). Here we have used the asymptotic formula

$$\begin{aligned} (\pi - \alpha)/\sqrt{6} &\sim 3\lambda(1 + \cos \theta)^{1/2} - (69/4)\lambda^3(1 + \cos \theta)^{3/2} \\ &+ (20481/160)\lambda^5(1 + \cos \theta)^{5/2} + \dots \quad (\theta \rightarrow \pi \text{ and } \beta_1 = \beta_2). \end{aligned} \quad (34)$$

In conclusion we have shown that in infinite polyacenacene the equilibrium configuration exhibiting glide plane symmetry is one of stable equilibrium, in which the C—C bonds of three chains all have the same length (1.413 Å) and are slightly shorter than the cross bonds (1.433 Å). This stable equilibrium configuration has zero gap and zero slope at the Fermi level. The conclusion that no bond alternation is expected in infinite

polyacene agrees with the work of Yamabe *et al* [10], where the one-dimensional tight-binding SCF MO method is used at the level of the CNDO/2 approximation. In the present investigation, however, the Coulomb interactions are not explicitly included. In a study of the Coulomb effects on polyacene, O'Connor and Watts-Tobin [14] stated: 'It appears that it is necessary to take careful account of the Coulomb interaction between the  $\pi$  electrons.' From this consideration, more sophisticated approaches would be required for further investigation of the electronic structure of polyacene. Work in this direction is in progress.

## References

- [1] Little W A 1964 *Phys. Rev.* **134** 1416
- [2] Ginzburg V L 1970 *Sov. Phys.-Usp.* **13** 335
- [3] Peierls R 1955 *Quantum Theory of Solids* (Oxford: Oxford University Press) p 108
- [4] Longuet-Higgins H C and Salem L 1959 *Proc. R. Soc. A* **251** 172
- [5] Salem L and Longuet-Higgins H C 1960 *Proc. R. Soc. A* **255** 435
- [6] Wangbo M-H, Hoffmann R and Woodward R B 1979 *Proc. R. Soc. A* **366** 23
- [7] Tanaka K, Ohzeki K, Nankai S, Yamabe T and Shirakawa H 1983 *J. Phys. Chem. Solids* **44** 1069
- [8] Kivelson S and Chapman O L 1983 *Phys. Rev. B* **28** 7236
- [9] Kimura M, Kauabe H, Nishikawa K and Aono S 1986 *J. Chem. Phys.* **85** 3090
- [10] Yamabe T, Tanaka K, Ohzeki K and Yata S 1982 *Solid State Commun.* **44** 823
- [11] Terao T, Maeda S, Yamabe T, Ohzeki K and Yata S 1982 *Proc. Ann. Meet. of the Physical Society of Japan (Yokohama)* vol 2 p 308 (31p-k-1)
- [12] Born M and von Karman T 1912 *Z. Phys.* **13** 297
- [13] Parry D E and Thomas J M 1975 *J. Phys. C: Solid State Phys.* **8** L45
- [14] O'Connor M P and Watts-Tobin R J 1988 *J. Phys. C: Solid State Phys.* **21** 825