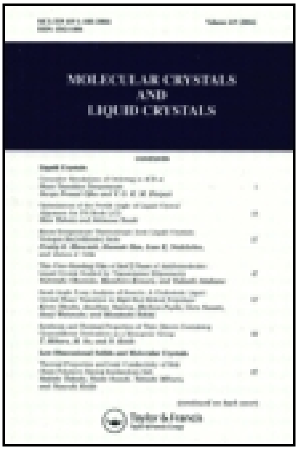

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Electronic Structures of Conjugated Polymers and Conducting Mechanism

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ELECTRONIC STRUCTURES OF CONJUGATED POLYMERS AND CONDUCTING MECHANISM

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Abstract Concerning the conduction mechanism of conjugated polymers, two selected subjects are studied. First, the occurrence of the counter-Peierls distortion in the heavily doped trans-polyacetylene of p-type is pointed by the semiempirical Hartree-Fock crystal orbital calculation. Second, the energy balance of bipolaron separation in several conjugated polymers are discussed.

INTRODUCTION

Electric conduction mechanism is one of the fundamental problem in the study of solid state properties of electrically conductive polymers. In the present article we like to discuss two specific subjects related with this theme for conjugated organic polymers doped with electronic acceptors. The first subject deals with the lattice distortion in the heavily-doped trans-polyacetylene(PA) based on the crystal orbital calculation. In the second subject the energy balance of bipolaron depending on the separation distance is to be discussed in a qualitative manner.

COUNTER-PEIERLS DISTORTION IN HEAVILY-DOPED PA

It has often been referred to that polaron and charged soliton are responsible for the conduction carrier in the lightly-doped trans-PA mainly on the basis of the analysis of temperature-dependent magnetic susceptibility.[1,2] In this section we pay attention mostly to the trans skeleton, which is known as the structural phase of the doped PA,[3] and, hence, drop the prefix trans.

In the heavily-doped regime (in excess of 7 molar % of the dopant concentration) the tails of adjacent charged solitons begin to overlap, as we employ a picture in which each tail (the spatial halfwidth of the kink) of a charged soliton extends over seven carbon sites.[4] Hence one can expect the relaxation of the bond alternation, ending up as the trans-regular chain illustrated in Figure 1(C). This "counter"-Peierls distortion will give rise to a metallic state corresponding to the outset of Pauli susceptibility in this regime.[5] Actually, however, the possibility of this relaxation should be checked with a viewpoint of energetical stabilization.

Brédas et al.[6] first predicted equal C-C bond lengths in the calculation of $(C_6H_6Li_2)_x$. Kertész et al.[7] have examined this tendency with the use of the extended Hückel crystal orbital (CO) calculation to find the vanishment of the bond alternation in the model for heavily-doped PA. However, the extended Hückel scheme does not include the internuclear repulsion terms, and hence there remains still some ambiguity with respect to their result.

Therefore, in this section, we re-examine the electronic structure of the model for heavily-doped PA (20 molar %) of p-type with the use of the semi-empirical Hartree-Fock CO method under the level of the CNDO/2 approximation.[8] Three kinds of structural isomers of $(CH)^{+0.2}{}_x$ in Figure 1 are considered for the model calculation provided that a dopant molecule withdraws an electron. The unit cell employed for (A) is $(C_{10}H_{10})^{+2}$ and those for (B) and (C) $(C_5H_5)^+$. The intercell interactions are considered as far as the 2nd and the 4th nearest neighbor cells for (A) and for (B) and (C), respectively. The bond lengths and angles are employed from the results of the undoped PA.[9] The original structure of the undoped PA is reserved in (A), whereas the location of the charged soliton is emphasized in (B). (C) is the regular form without bond alternation.

The stability of the isomers is in the order of (C)>(B)>(A) as listed in Table I. In Figure 2 are shown the π-band structures obtained for these isomers. It is seen that the band gap disappears in (A) and (C). In (B), however, there remains a finite band gap since this structure is essentially a pentamerized version of PA. This result supports the occurrence of the counter-Peierls distortion leading to the structure (C). Thus the CDW instability caused in the undoped PA no more manifested itself in the heavily-doped PA. This tendency is also confirmed down to the case of 9

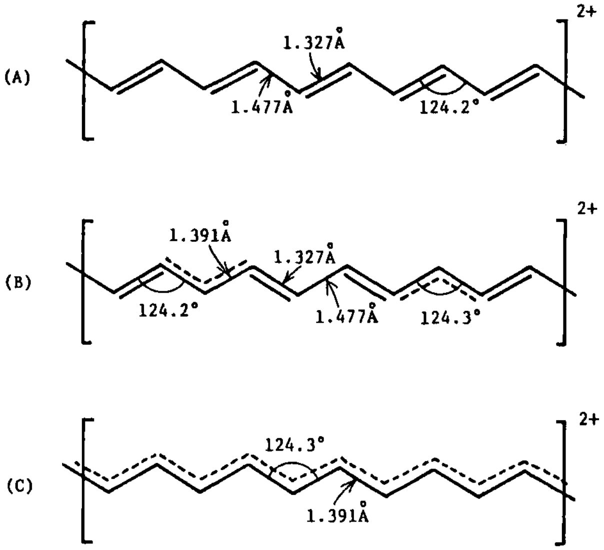


FIGURE 1 Structural isomers of $(CH)^{+0.2}_x$.

TABLE I Calculated data for the three isomers of $(CH)^{+0.2}_x$.

	Relative energy(in eV/$(CH)^{+0.2}$)	Band gap (in eV)
A	0.315	0
B	0.036	6.41
C	0	0

molar % of the dopant concentration as shown in Table II. In the low temperature, however, the gapless metallic state (C) may be deformed into the state (C') with small band gap caused by the coupling with vibrations which are frozen.

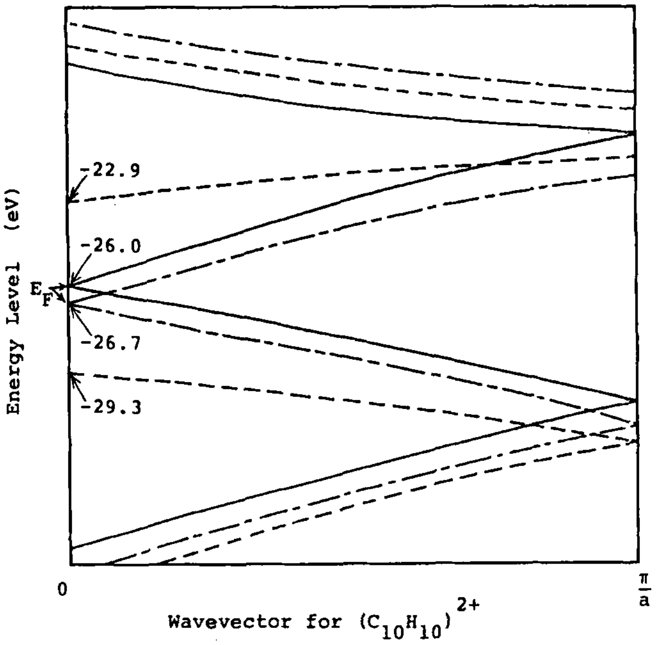


FIGURE 2 π-band structures near the Fermi level(E_F) of the three isomers of $(CH)^{+0.2}_x$: (A)—·— (B)-----(C)—— in Figure 1.

TABLE II Relative energy (in eV/$(CH)^{+\delta}$) of the two isomers of $(CH)^{+0.14}_x \sim (CH)^{+0.09}_x$.

	$(CH)^{+0.14}_x$	$(CH)^{+0.11}_x$	$(CH)^{+0.09}_x$
B	0.016	0.017	0.016
C	0	0	0

Similar check has been performed with respect to the isomers of the <u>cis</u>-$(CH)^{+0.2}_x$ in Figure 3. This is rather a fictitious model since the doped-PA necessarily isomerizes into the <u>trans</u>-skelton as mentioned above. The structure (B) would be unrealistic because the normal distance between two charged solitons in the <u>cis</u>-PA has been estimated to be <u>ca</u>. 26Å,[10] and hence gives very high energy probably because of strong Coulomb repulsion between localized positive charge. The structure (C) is calculated to be

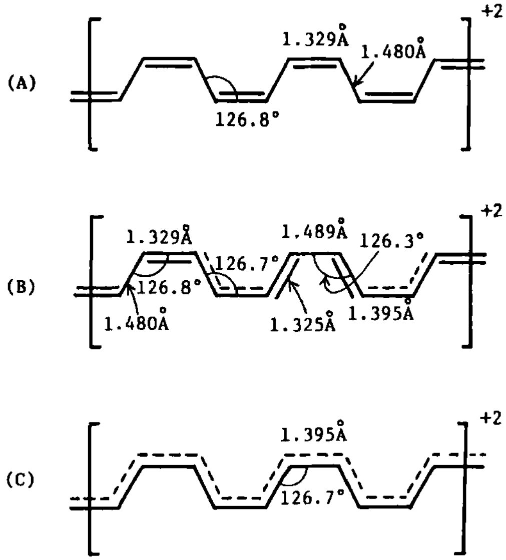


FIGURE 3 Structural isomers of <u>cis</u>-$(CH)^{+0.2}_x$.

TABLE III Calculated data for the two isomers of <u>cis</u>-$(CH)^{+0.2}_x$.

	Relative energy(in eV/$(CH)^{+0.2}$)	Band gap (in eV)
A	0.281	0
C	0	0

more stable than the structure (A) as is seen in Table III, suggesting again the vanishment of the bond alternation even in the <u>cis</u>-PA. Both have zero gap, as previous.

ENERGY BALANCE OF BIPOLARON SEPARATION

In doped conjugated polymers consisting of connected aromatic rings such as poly(*p*-phenylene) (PPP), polypyrrole (PPy) and so on, the conduction carrier has been interpreted in terms of bipolaron.[6,11] A bipolaron is formed by two polarons spatially correlated with the separation *R*, resulting in a singlet spin state as illustrated in Figure 4(A). Generally, A and A' are structural isomers as shown in Table IV, A being energetically more stable unit. In this

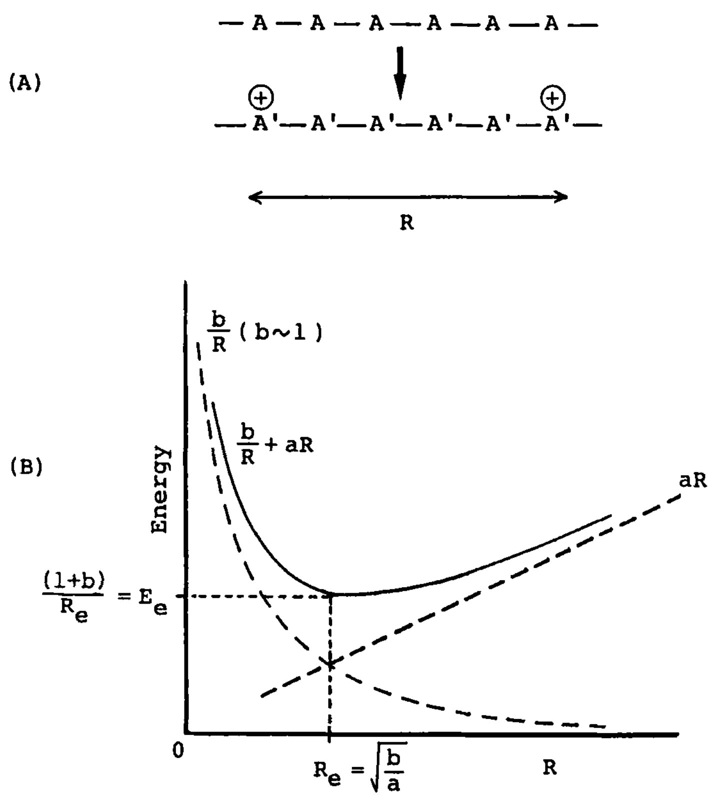
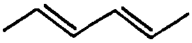
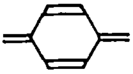
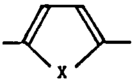
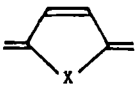


FIGURE 4 Schematic representation for energy balance of bipolaron(see text).

sense, if *R* is large, the energy is destabilized as indicated by the dashed straight line in Figure 4(B), where the gradient *a* corresponds roughly to the energy difference between A and A' listed in Table IV. On the other hand, the Coulomb repulsion energy between two charges can be drawn by the dashed curve line, *b* (∿1) standing for the screening effect between two charges. Hence, apart from the electronic energy of each polaron being *R*-independent, the energy balance of bipolaron separation can be roughly estimated by the summation of the above two terms as expressed by the solid line in Figure 4(B).

The optimal distance R_e is hence proportional to the square root of *b* and of the inverse of *a*. Therefore, it is obvious that the large energy difference between A and A' (isomerization energy from A to A') causes the short bipolaron separation, which is consistent with the results of the calculation listed in Table IV.

TABLE IV Calculated energy difference between stable(A) and quasi-stable(A') structure, ΔE, along with the distance of bipolaron separation, R.

A	A'	E ∿a (in eV/unit)	R
		0	∞ (as two charged solitons; Ref.4)
		0.1	26Å (Ref.10)
		0.3	15∿20Å (Refs. 6,12)
		0.4(X=N) 0.2(X=S)	7∿8Å (Ref.12)

CONCLUDING REMARKS

We have studied the counter-Peierls distortion in PA. It will be of importance further to investigate the transport problem in the lattice thus formed. The discussion in the latter half gives a simple insight into the bipolaron separation.

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