RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 32, NUMBER 6 15 SEPTEMBER 1985

Design of novel polymers with metallic conductivity: Polyazacetylene and polyboracetylene

Kazuyoshi Tanaka, Katsuya Ueda, Tsuneaki Koike, Masanori Ando, and Tokio Yamabe*
Department of Hydrocarbon Chemistry, Faculty of Engineering and Division of
Molecular Engineering, Graduate School of Engineering,
Kyoto University, Sakyo-ku, Kyoto 606, Japan
(Received 16 April 1985)

With a basis on the idea of controlling the number of π electrons in the polymer skeleton, we have theoretically designed novel polymers, polyazacetylene and polyboracetylene, that will show metallic conductivity without doping. Examination of the electronic structures of these polymers in planar geometries shows that they have no band gap between the valence and conduction bands.

Much effort has been devoted to experimental and theoretical investigations of electrically conductive polymers. Almost all of these polymers have a finite band gap in the pristine state and hence should be doped with relevant electron acceptors or donors for the manifestation of high conductivity.[1] Hence, it would also be of interest to propose new polymers which already show metallic conductivity *per se* without the doping process. Such polymers should have zero band gap between the valence and the conduction bands. Polythiazyl, $(SN)_x$, is the sole example that satisfies this condition in actually existing polymers.[2]

In this Rapid Communication, we would like to report a design of novel polymers with metallic conductivity and check their electronic structures to confirm that they have zero band gap. The basic idea of the present design lies in the control of the number of π electrons in the skeleton of polyacetylene (PA) by introducing heteroatoms therein. It will be useful to briefly review here the electronic structure of *trans*-PA.

Regular *trans*-PA in Fig. 1(a) has in its unit cell one π electron, so that the total π band is half filled. Hence, *trans*-PA in this geometry has zero band gap and will show a metallic conductivity. However, it is well known that this polymer skeleton spontaneously deforms into the dimerized geometry with C—C bond alternations [Fig. 1(b)] to achieve energetic stabilization,[3] which is often termed a Peierls distortion[4] or as the generation of a charge-density wave (CDW).[5] As a result, *trans*-PA becomes an insulator with a finite band gap since its new unit cell provides the whole polymer chain with two π electrons.

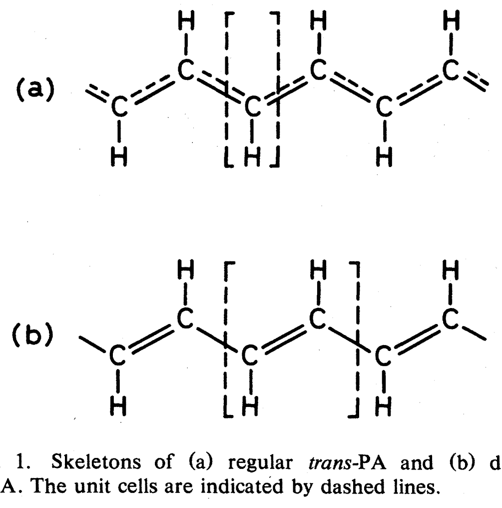

FIG. 1. Skeletons of (a) regular *trans*-PA and (b) dimerized *trans*-PA. The unit cells are indicated by dashed lines.

Here we use the above guiding principle to design the nitrogen- and boron-substituted PA illustrated in Fig. 2, termed polyazacetylene (PAzA) and polyboracetylene (PBA), respectively. In PAzA it is expected that two π electrons are supplied from each trivalent nitrogen atom. On the other hand, in PBA no π electrons will be contributed from boron atoms. Therefore, the number of π electrons per CHNH and CHBH unit will vary from three to unity, respectively, which leads to closure of the band gap of these polymers as long as CHNH and CHBH can be the unit cells thereof and the chains are kept planar.

In order to assess the above prospect, we have performed calculations of the band structures of PAzA and PBA with the use of the one-dimensional tight-binding self-consistent-field–crystal-orbital method (SCF-CO) at the CNDO/2 (complete neglect of differential overlap, parametrization scheme No. 2) level[6] including all the valence electrons. This version has been successfully applied to the calculations of the electronic structures of PA[3,7]

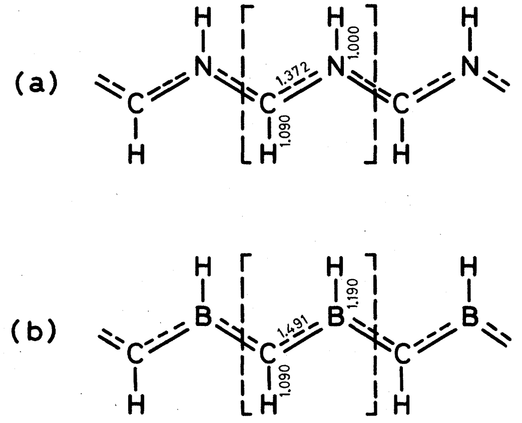

FIG. 2. Skeletons of (a) PAzA and (b) PBA with bond lengths in Å. Indicated are the formal unit cells required from symmetry. Those which are actually employed for the calculation consist of the double size of the formal unit cells, that is $(CHNH)_2$ and $(CHBH)_2$ (see text).

and its fluorinated derivatives[8] as well as to several polymers consisting of condensed aromatic rings.[9] For computational reasons, the unit cell employed here consists of $(CHNH)_2$ or $(CHBH)_2$. The number of representative wave vectors is chosen as 21 with regular intervals in the Brillouin zone. The overlap and the electron repulsion integrals are considered as far as the fourth neighboring cell (about 20 Å from the central unit cell).

The point of the assessment lies in the confirmation of the number of π electrons supplied from a nitrogen or a boron atom embedded in the polymer chain. We consider the unit cell of the polymer to be CHNH or CHBH, the reason for which is to be mentioned later. There can be a combination of two kinds of the C—N (or C—B) bond lengths, such as C—N and C=N, in this unit cell like in dimerized *trans*-PA [see Fig. 1(b)]. These two variables are optimized so as to achieve the most stable geometries from the energetic point of view assuming planarity of the polymer chains. This assumption seems to be plausible from the argument about the nature of the local atomic geometry.[10] Each C—N (or C—B) bond length is changed independently with a mesh of 0.001 Å in order to find the best combination of the two variables. All of the bond angles are kept at 120° (sp^2 hybridization angle) and the C—H and N—H (or B—H) bond lengths are fixed to be the standard values.[10]

It is seen in Fig. 2 that there are no bond alternations in both PAzA and PBA chains after the energetic optimization. This is rather surprising, but is reminiscent of the vanishing of the bond alternations in heavily doped PA, that achieves a metallic conductivity.[11] Moreover, this feature seems to be connected with the fact that one cannot draw ordinary chemical bonds satisfying the octet rule in both polymers, being similar to the case of polythiazyl.

The calculated electronic properties of PAzA and PBA in the optimized geometries are listed in Table I along with those of *trans*-PA for the sake of comparison. The distribution of π-electron densities after the SCF-CO calculation assures that a nitrogen and a boron atom provide the system with two and no π electrons, respectively. Therefore, there is no band gap in the band structures of both polymers (Fig. 3) due to sticking of the HO (highest occupied) and the LU (lowest unoccupied) bands, as is rigorously required from the symmetry of polymer chains.[12] Note that the bond alternations with a combination of two kinds of C—N (or C—B) bond lengths *cannot* separate the HO and the LU bands since the unit cell remains CHNH (or CHBH) in such bond-alternant chain.

TABLE I. Electronic properties of PAzA, PBA, and *trans*-PA (from Ref. 8).

	PAzA	PBA	*trans*-PA
π-electron densities (units of $\lvert e \rvert$)	C: 1.42 N: 1.58	C: 0.48 B: 0.52	C: 1.00
HO π-band width (eV)	7.86	8.25	15.55
LU π-band width (eV)	5.25	11.41	9.70
Ionization potential (eV)	0.52	11.39	7.82
Electron affinity (eV)	0.52	11.39	0.36
Density of states at the Fermi level[a]	0.07	0.05	0
Effective mass at the Fermi level[b]	$-0.82m_0$	$0.68m_0$	. . .

[a] In units of states/eV (CHNH) or states/eV (CHBH).

[b] m_0 signifies the mass of a free electron.

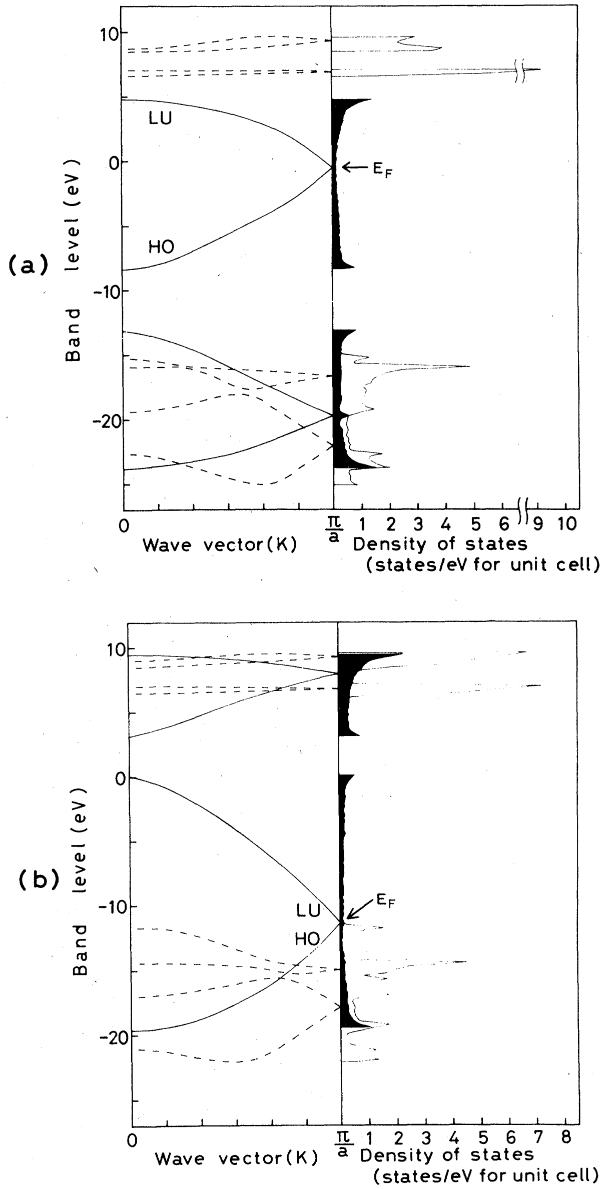

FIG. 3. The band structures of (a) PAzA and (b) PBA with the density of states and its component of π nature (shadowed area). Dashed and solid lines indicate σ and π bands, respectively, and E_F denotes the Fermi level. The values of a are 4.753 and 5.165 Å in (a) and (b), respectively.

Application of the formal argument for Peierls distortion in a purely one-dimensional system[4] requires, e.g., dimerization of the present unit cell. The dimerized unit cell (CHNHCHNH or CHBHCHBH) should involve at least three different kinds of C—N (or C—B) bond lengths, which is rather unusual from the ordinary chemical point of view. Hence, we believe that the vibronic matrix element leading to this dimerization would be small or virtually zero, as in the case of polythiazyl $(SN)_x$, the unit cell of which consists of SN having three π electrons.[13] Furthermore, such dimerization in PAzA and PBA ought to undertake a considerable decrease in entropy at room temperature. Hence, manifestation of metallic conductivity in PAzA and PBA is promising at the higher-temperature range.

It is also seen from Table I that the small ionization potential of PAzA suggests a high efficiency of *p*-type doping for this material, whereas *n*-type doping seems to work well for PBA with a large electron affinity. Furthermore, doping of PAzA and PBA with electron acceptors and donors, respectively, will promote the planarity of these chains owing to the possible existence of cationic trivalent nitrogen or anionic trivalent boron atoms, being isoelectronic with sp^2 hybridized carbon atoms in a PA chain.

In summary, we have designed PAzA and PBA as new candidates of polymers with metallic conductivity already in their pristine states under the condition that the polymer chains are planar. Even if this condition is not satisfied, *p*-type doping of PAzA or *n*-type doping of PBA will recover the planarity of the polymer chain. Incidentally, it is also of interest to note that incorporation of a few molar percent of CHNH or CHBH unit in the skeleton of *trans*-PA will make this polymer conductive. This may open up a new category of such conductive polymers which already have the dopants inside their skeletons.

Actual synthesis of these polymers is of obvious interest. A more detailed investigation from both theoretical and experimental points of view is now planned and will be reported in the near future.

This work was partially supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science and Culture of Japan and by the Asahi Glass Foundation for Industrial Technology. Numerical calculations were carried out at the Data Processing Center of Kyoto University and the Computer Center of Institute for Molecular Science.

---

[*] Also at Institute for Fundamental Chemistry, 15 Morimoto-cho, Shimogamo, Sakyo-ku, Kyoto 606, Japan.

[1] See, e.g., A. J. Heeger and A. G. MacDiarmid, in *The Physics and Chemistry of Low Dimensional Solids,* edited by L. Alcacer (Reidel, Dordrecht, 1980), p. 353; R. H. Baughman, J. L. Brédas, R. R. Chance, H. Eckhardt, R. L. Elsenbaumer, D. M. Ivory, G. G. Miller, A. F. Preiziosi, and L. W. Shacklette, in *Conductive Polymers,* edited by R. B. Seymour (Plenum, New York, 1981), p. 137.

[2] A. Zunger, J. Chem. Phys. **63**, 4854 (1975); C. Merkel and J. Ladik, Phys. Lett. **56A**, 395 (1976); T. Yamabe, K. Tanaka, A. Imamura, H. Kato, and K. Fukui, Bull. Chem. Soc. Jpn. **50**, 798 (1977).

[3] T. Yamabe, K. Tanaka, H. Terama-e, K. Fukui, A. Imamura, H. Shirakawa, and S. Ikeda, J. Phys. C **12**, L257 (1979); A. Karpfen and R. Höller, Solid State Commun. **37**, 179 (1981).

[4] R. E. Peierls, *Quantum Theory of Solids* (Oxford Univ. Press, London, 1955), Chap. 5.

[5] M. Kertész, J. Koller, and A. Ažman, J. Chem. Phys. **67**, 1180 (1977).

[6] A. Imamura and H. Fujita, J. Chem. Phys. **61**, 115 (1974).

[7] T. Yamabe, K. Tanaka, H. Terama-e, K. Fukui, A. Imamura, H. Shirakawa, and S. Ikeda, Solid State Commun. **29**, 329 (1979).

[8] T. Yamabe, K. Tanaka, H. Terama-e, K. Fukui, H. Shirakawa, and S. Ikeda, Synth. Met. **1**, 321 (1979/80).

[9] T. Yamabe, K. Tanaka, K. Ohzeki, and S. Yata, Solid State Commun. **44**, 823 (1982); K. Tanaka, K. Ohzeki, S. Nankai, T. Yamabe, and H. Shirakawa, J. Phys. Chem. Solids **44**, 1069 (1983); K. Tanaka, K. Ueda, T. Koike, and T. Yamabe, Solid State Commun. **51**, 943 (1984).

[10] J. A. Pople and D. L. Beveridge, *Approximate Molecular Orbital Theory* (McGraw-Hill, New York, 1970), Chap. 4.

[11] J. L. Brédas, R. R. Chance, and R. Silbey, J. Phys. Chem. **85**, 756 (1981); M. Kertész, F. Vonderviszt, and S. Pekker, Chem. Phys. Lett. **90**, 430 (1982); T. Yamabe, K. Tanaka, T. Koike, and M. Ueda, Mol. Cryst. Liq. Cryst. **117**, 185 (1985).

[12] See, e.g., V. Heine, *Group Theory in Quantum Mechanics* (Pergamon, London, 1960), p. 265.

[13] C. M. Mikulski, P. J. Russo, M. S. Saran, A. G. MacDiarmid, A. F. Garitó, and A. J. Heeger, J. Am. Chem. Soc. **97**, 6358 (1975).