Electronic Structure of Poly(dichlorophosphazene)

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ABSTRACT: The electronic structure of poly(dichlorophosphazene) (PDCP) has been studied by using the one-dimensional tight-binding SCF-CO (self-consistent field-crystal orbital) method. Eight kinds of conformational models previously proposed have been checked prior to the analyses. It has been found that PDCP favors the cis,trans conformation as a whole. The electronic structure, including the band structure, is examined in detail for the conformational model that is most plausible.

I. Introduction

Intensive studies of polyphosphazene (Figure 1a) with various kinds of side groups R have been performed experimentally with respect to their syntheses, structures, reactivities, and solid-state properties.[1-3] Most polyphosphazenes are good insulating, nonburning, and chemically stable materials, establishing a wide range of applications.[3] In recent years, on the other hand, interest is arising in newer functions such as electrical conductivity manifested in composite systems of polyphosphazenes. Examples include the formation of an ionic conducting complex consisting of poly[bis[2-(2-methoxyethoxy)ethoxy]phosphazene] with lithium trifluoromethanesulfonate[4] and the manifestation of photoconductive properties in poly[bis(*p*-tolylamino)phosphazene] or poly[bis(2-naphthoxy)phosphazene] doped with trinitrofluorenone.[5]

Poly(dichlorophosphazene) (PDCP; Figure 1b) is regarded as a fundamental member of the polyphosphazenes and is often used as an intermediate material to prepare poly(organophosphazene). The conformation of PDCP has been somewhat controversial. By means of X-ray diffraction analyses, the chain conformation of PDCP was considered to be regular helical on the one hand[6] and slightly distorted cis,trans planar on the other.[7] Characterization of the infrared spectrum of this polymer was consistent with the latter conformation.[8] Detailed structural analysis of highly purified PDCP based on the X-ray diffraction measurement has recently been attempted by Allcock, Arcus, and Stroh.[9] Examination of several possible models for PDCP conformation therein again favored a cis,trans planar chain, the chain repeat distance being 4.92 Å. This conclusion is similar to that for poly(difluorophosphazene).[10]

In this paper, we discuss the electronic structure of PDCP in view of the developing interest in electronic process related with solid-state properties of polyphosphazenes. Direct energetical calculations are performed with respect to the eight kinds of chain conformations of PDCP proposed in ref 9. The electronic structure of PDCP in the most plausible conformation thus predicted is examined in detail.

The method of calculation employed here is briefly outlined in section II. The energetic calculations for various conformational models are described in section III. The electronic structure of the most plausible conformation of PDCP is discussed in section IV.

II. Method of Calculation

The calculations were performed by employing the one-dimensional tight-binding SCF-CO (self consistent field-crystal orbital) method at the level of the CNDO/2 (complete neglect of differential overlap) approximation considering all the valence electrons.[11] This method has been yielding reliable results not only for organic polymers including polyacetylene,[12] polyacene,[13] and poly(vinylene sulfide)[14] but also for an inorganic conductive polymer, poly(sulfur nitride).[15] Eight conformational models proposed in ref 9 (naming of models A-H after ref 9 is employed throughout this paper) were calculated with ordinary sp basis set.[16] These models include regular or distorted cis,trans planar, helix, and twisted trans,trans conformations. For the most plausible model of PDCP selected from the energetical point of view, detailed analyses of electronic structure of this polymer were performed. Since a contribution of 3d atomic orbitals (AO's) of phosphorus atoms has been suspected,[3] the calculation including 3d AO's of P and Cl (spd basis set)[16] was also undertaken.

Number of representative wave vector K was chosen as 21 at regular intervals ($\pi/10a$; a is the length of the unit cell) in the Brillouin zone. The values of the overlap integrals and the electron repulsion integrals were considered as far as the fourth-nearest-neighboring cell (ca. 24 Å from the central cell). The density of states (DOS) was evaluated after the conventional method of histograms by Brust[17] from the interpolated energy bands with the use of the cubic spline functions.

Table I
Relative Stabilization Energies per ($N_2P_2Cl_4$) Cell of PDCP

model[a]	relative stabilization energies,[b] eV
A (cis,trans)	+1.544
B (distorted cis,trans)	+0.215
C (helix)	+6.805
D (trans,trans)	+5.238
E (cis,trans)	+12.277
F (helix)	+15.506
G (trans,trans)	+15.275
H (cis,trans)	0.0

[a] Naming after ref 9 (see text). [b] Energies are given relative to model H, where the positive value signifies the unstabilization.

III. Energetical Calculation

Relative stabilization energies of the eight kinds of chain conformations in ref 9 are listed in Table I. It is seen that the cis,trans or distorted cis,trans conformations such as H, B, and A are stable (E is an exception). The helix and trans,trans conformations are unstable as a whole. That the model E is unstable can be attributed to rather large bond angles at nitrogen atoms (141.5°) in this model, which are required to fit the chain repeat distance 4.92 Å.

Although a full optimization of the bond lengths and the angles has not been attempted here, it seems probable that the cis,trans or distorted cis,trans conformation well represents the skeleton of PDCP, which is consistent with

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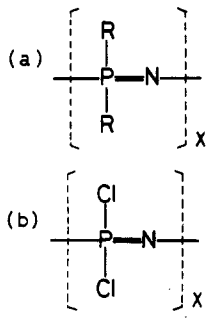

Figure 1. Schematic drawing of (a) general polyphosphazene and (b) poly(dichlorophosphazene).

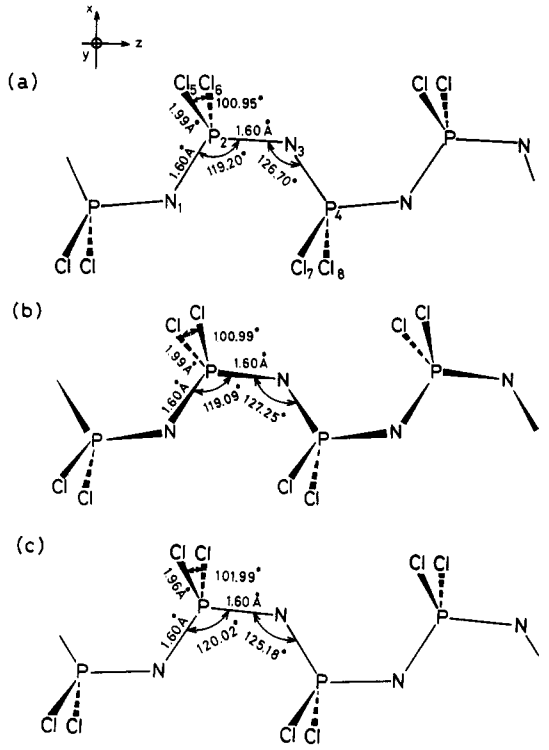

Figure 2. (a) Coordinate axes and cis,trans conformational model H employed in the present electronic structure analysis. (b) Model B. (c) Model A. All of the bond lengths and the bond angles are calculated from the Cartesian coordinates in ref 9.

most experimental predictions.[7-9] The most plausible conformational model H is illustrated in Figure 2. However, models B and A also shown there should not be neglected since these could contribute to the skeleton of PDCP as metastable conformations in addition to model H, among which the actual skeleton of PDCP changes. Such situation may correlate with disorder of the system found even in highly purified PDCP by the X-ray diffraction measurement.[9] In the next section the electronic structure of PDCP is to be analyzed in detail mainly with respect to the conformational model H.

IV. Electronic Structure

The band structure of PDCP is shown in Figure 3 along with the DOS. Since the symmetry group of the conformational model H is isomorphous with C_s, the bands are classified into two representations A′ (σ type) and A″ (π type) after the conventional line-group theory.[18] Both the highest occupied (HO) and the lowest unoccupied (LU) bands are of σ nature. The next HO (NHO) band tangled with the HO band is of π nature. The lowest point in the LU band lies almost in the middle of the Brillouin zone. Hence the minimum interband transition from the HO to the LU band ($\sigma \rightarrow \sigma^*$) is indirect.

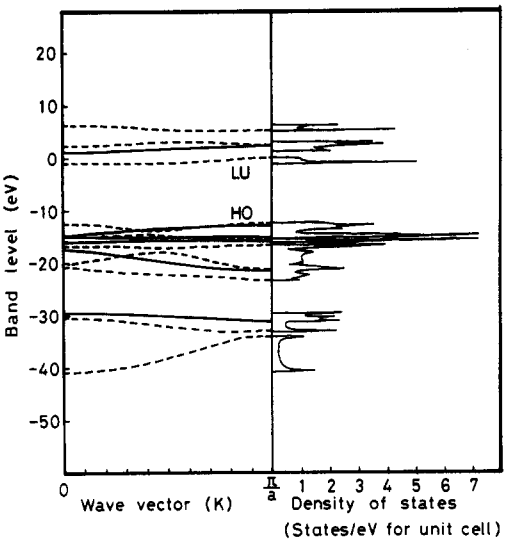

Figure 3. Band structure and density of states (DOS) of PDCP. Representations of broken and solid lines are A′ and A″, respectively. The value of a is 2.46 Å since the unit cell consists of $PNCl_2$ in model H.

Table II
Parameters of Electronic Properties Induced from the Band Structures

	model H	model B	model A
ionization potential,[a] eV	12.53 (13.00)	12.50	12.43 (13.01)
electron affinity, eV	0.95	0.99	0.77
HO band width,[a] eV	1.33 (1.75)	1.14	1.33 (1.75)
LU band width, eV	0.93	1.04	0.92
band gap,[a] eV	11.59 (12.05)[b]	11.51	11.67 (12.24)[b]

[a] Values in parentheses are those for the NHO bands. [b] Transition energy from the NHO to the LU band.

The band gap is large, as shown in Table II, being almost the same as that of poly(vinylene sulfide) under the same method of calculation.[14] Since the Hartree–Fock type SCF–CO scheme, on which the present method is based, has a tendency toward overestimation of the band gap,[19] the actual value of this quantity is to be somewhat reduced. In any case, this result suggests that PDCP is a good electrically insulating material.

It is noted that other cis,trans conformational models have almost the same values of these parameters (Table II) induced from the band structure. The width of the HO and the LU bands are small as a whole, indicating that electrons in this polymer skeleton do not appreciably delocalize.

It may be possible to get higher electrical conductivity in PDCP with p-type dopants utilizing the nature of the NHO π band. An n-type doping, however, will not be effective due to the σ nature of the LU band. One could also argue that an increase in the electrical conductivity or a manifestation of photoconductivity in doped poly[bis(*p*-tolylamino)phosphazene] or poly[bis(2-naphthoxy)phosphazene][5] originates from the carrier hopping among the side groups as in the case of doped poly(*N*-vinylcarbazole).[20] Under such a situation π bands occurring from the side groups (*p*-tolylamino or naphthoxy) will appear above the present HO band.

The orbital patterns of the highest occupied crystal orbital (HOCO) and the next highest occupied crystal obital (NHOCO) are shown in Figure 4. In both patterns of the HOCO and the NHOCO, 2p AO's of nitrogen atoms are dominant, with a smaller contribution of 3p AO's of chlorine atoms. Hence these patterns represent lone-pair orbitals of nitrogen atoms. The LUCO pattern mainly distributes on 3s AO of phosphorus atoms, although it is

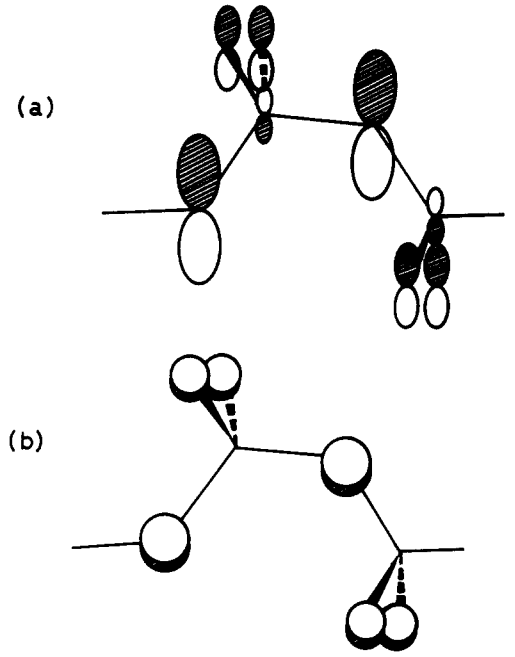

Figure 4. Orbital patterns of (a) the HOCO and (b) the NHOCO.

Table III
AO Densities and Atomic Net Charges

	atoms		
	P	N	Cl
AO density[a,b]			
s	1.287 (0.994)	1.546 (1.422)	1.902 (1.873)
p_x	0.877 (0.624)	1.210 (1.232)	1.794 (1.677)
p_y (p_π)	0.787 (0.621)	1.843 (1.314)	1.619 (1.541)
p_z	1.008 (0.644)	0.957 (1.226)	1.929 (1.801)
$3d_{z^2}$	(0.385)		(0.020)
$3d_{xz}$	(0.389)		(0.021)
$3d_{yz}$ (d_π)	(0.376)		(0.029)
$3d_{x^2-y^2}$	(0.314)		(0.044)
$3d_{xy}$ (d_π)	(0.379)		(0.034)
atomic net charge[a]	+1.042 (+0.275)	−0.556 (−0.194)	−0.243 (−0.041)

[a] Values in parentheses are those obtained with the inclusion of 3d AO's of P and Cl. [b] For the coordinate axes, see Figure 2.

not illustrated in Figure 4 due to the complex number of coefficients of the LUCO.

The AO densities and atomic net charges in the conformational model H are listed in Table III. Values of those in the models B and A are almost the same. It is seen that phosphorus and nitrogen atoms bear positive and negative charges, respectively, being consistent with experimental observation of a strong infrared absorption peak due to the P–N stretching mode.[8] Polarization on each atom, however, is relaxed to a certain extent by inclusion of 3d AO's in the basis set. It is noted that the contribution of 3d AO's of phosphorus atoms are considerably large compared with those of chlorine atoms. This seems to stem from the fact that phosphorus atoms cannot satisfy the usual octet rule. Hence, from the viewpoint of the valence-bond picture, the electronic state of PDCP is described by a linear combination of such structures as shown in Figure 5.

The values of π bond orders between phosphorus and nitrogen p_π AO's listed in Table IV are not so large as, say, those of the usual C=C and C—C π bond orders in polyacetylene (0.847 and 0.399, respectively[12]). Participation of 3d AO's considerably increases the total π bond orders. Therefore, as was previously suspected,[3] the contribution from the p_π–d_π interaction in PDCP is not negligible.

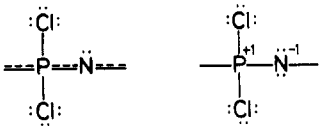

Figure 5. Possible valence-bond structures for PDCP.

Table IV
π Bond Orders[a]

atoms	combination of π AO's	without 3d AO's	including 3d AO's
N_1–P_2	$2p_y$–$3p_y$	0.304	0.339
	$2p_y$–$3d_{yz}$	0.0	−0.256[b]
	$2p_y$–$3d_{xy}$	0.0	−0.475[b]
P_2–N_3	$3p_y$–$2p_y$	0.305	0.348
	$3d_{yz}$–$2p_y$	0.0	0.523
	$3d_{xy}$–$2p_y$	0.0	−0.099[b]

[a] For the numbering of atoms and coordinate axes, see Figure 2. [b] Bonding nature. Minus sign comes from the orientation of d_π AO's.

V. Concluding Remarks

The electronic structure of PDCP has been studied on the basis of the tight-binding SCF–CO method. There are four major features in the present study:

(1) Cis,trans conformations are energetically stable. There is not any significant difference in electronic structures of PDCP chains in this kind of conformation.

(2) The band structure suggests that rather strong p-type dopant will be effective for the increase of electrical conductivity of PDCP.

(3) The P–N bonds are rather polarized, phosphorus atoms being positively charged.

(4) Interactions between phosphorus $3d_\pi$ and nitrogen $2p_\pi$ AO's are not negligible.

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