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The Electronic States of $(SN)_x$ and $(SCH)_x$ Polymers

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One-dimensional $(SN)_x$ and its isoelectronic system $(SCH)_x$ polymers are treated on the basis of the SCF-tight-binding MO theory. The Pennsylvania structure of $(SN)_x$ has been shown energetically favorable comparing the Lyon structure. Judging from the state density at the Fermi level of $(SCH)_x$, it may be expected to be a metallic conductor under some favorable condition.

There have been considerable experimental and theoretical interests in low-dimensional metallic conductors such as tetracyanoquinodimethane (TCNQ) charge-transfer salts and $K_2[Pt(CN)_4]Br_{0.3}\cdot 3H_2O$ mixed valence complex.1) Recently, the third member, polymeric sulfur nitride, $(SN)_x$, has been revealed as a low-dimensional metallic polymer,2) which does not show the Peierls transition like the above two, and even becomes a superconductor at $\approx$0.3 K.3)

The theoretical band structure calculations of $(SN)_x$ have been performed with the OPW method4) and several non SCF-tight-binding techniques such as the extended Hückel method.5) In these tight-binding MO calculations, however, the electron-electron interaction potential is not taken into account explicitly, and hence these methods would be only reliable on the non-polar polymers such as polyethylene.6) Since the sulfur-nitrogen bond in $(SN)_x$ has been estimated experimentally to be of rather polar character,7) it would be suitable to calculate the MO including the electron repulsion integrals for this polymer. The SCF-tight-binding MO calculation including these repulsion integrals has been carried out only by Zunger and by Merkel and Ladik8) for the one-dimensional structure of $(SN)_x$ in the crystal structure proposed by Boudeulle and Michel (Lyon structure)9) based on the electron-diffraction analysis as shown in Fig. 1(A). The band structures obtained by them clearly show the metallic nature of $(SN)_x$, and the possibility of the occurrence of the Peierls transition has been denied by the former.

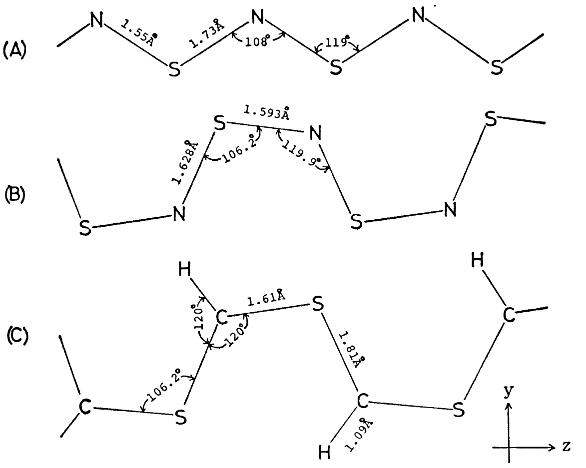


Fig. 1. The structures of $(SN)_x$ and $(SCH)_x$; (A) the Lyon structure (Ref. 9), (B) the Pennsylvania structure (Ref. 10), and (C) an assumed structure for the calculation here (see text).

More recently, however, the more reliable structure of $(SN)_x$ has been proposed by MacDiarmid *et al.* (Pennsylvania structure)10) based on the X-ray diffraction analysis as shown in Fig. 1(B). In this paper, we present the result of electronic states of the one-dimensional Pennsylvania structure of $(SN)_x$ by the SCF-tight-binding MO calculation including the electron repulsion, and, furthermore, the calculation for an assumed structure of $(SCH)_x$ polymer has been made so as to study an isoelectronic system with the $(SN)_x$ polymer.

Method of Calculation

In order to avoid the complicated calculations of the all matrix elements by *ab initio* methods, we employ the CNDO/2 approximation by Pople and Segal11) as Zunger did. The SCF iteration process is accelerated by the density matrix method previously introduced by Imamura and Fujita to calculate biopolymers.12) The formalism of the calculation has been described thoroughly in their article, so we will not mention the details here again. All valence AOs and 3d orbitals for sulfur atoms were considered since it has been pointed out that the contribution from 3d orbitals is not negligible for $(SN)_x$.8) For the parametrizations were adopted those of spd set by Santry and Segal,13) and the 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.

We assumed the structure of $(SCH)_x$ to be analogous to that of the Pennsylvania structure of $(SN)_x$, as shown in Fig. 1(C). The angle at sulfur was chosen as 106.2° after that in $(SN)_x$, and that at carbon as 120° after ordinary sp^2 hybridization. The two kinds of S–C bond distance, 1.81 and 1.61 Å, are employed from the data for dimethyl disulfide14) and thioformaldehyde,15) respectively. The C–H bond distance, 1.09 Å, also from the latter. Each of SN and SCH units consists of 11 valence electrons and, hence, an open-shell structure. Since the $(SN)_x$ crystal, however, does not show paramagnetism,10) the system could be treated as a closed-shell system. We employed $(SN)_2$ as a unit cell in the MO calculation of the $(SN)_x$ polymer. We also assumed $(SCH)_2$ as a unit cell in the $(SCH)_x$ polymer. Since the polymer chains possess a two-fold screw rotation as a symmetry operation, all pairs of bands stick together at the edges of the Brillouin zone,16) and in this case, the HOMO(π) and the LUMO(π^*) bands

Table 1. AO densities, atomic net charges, and the total energies of $(SN)_x$ and $(SCH)_x$

		$(SN)_x$: Pennsylvania structure		$(SN)_x$: Lyon structure[a]		$(SCH)_x$		
		S	N	S	N	S	C	H
AO	s	1.810	1.550	1.824	1.549	1.768	1.114	0.912
	p_x	1.407	1.218	0.714	1.163	1.478	1.135	
	p_y	0.822	1.235	0.784	1.315	0.923	0.962	
	p_z	0.728	1.228	1.497	1.153	0.929	0.964	
	d_{xz}	0.242		0.308		0.296		
	d_{xy}	0.133		0.219		0.091		
	d_{yz}	0.290		0.044		0.202		
	$d_{x^2-y^2}$	0.087		0.326		0.065		
	d_{z^2}	0.250		0.098		0.160		
π Electron densities		1.782	1.218	1.947	1.153	1.865	1.135	
Atomic net charges		+0.231	−0.231	+0.186	−0.186	+0.087	−0.175	+0.088
Total energies per unit cell (in eV)		−1230.056 (−1218.220)[b] (−1227.731)[c]		−1228.562[d]			−1018.057 (−1005.877)[b]	

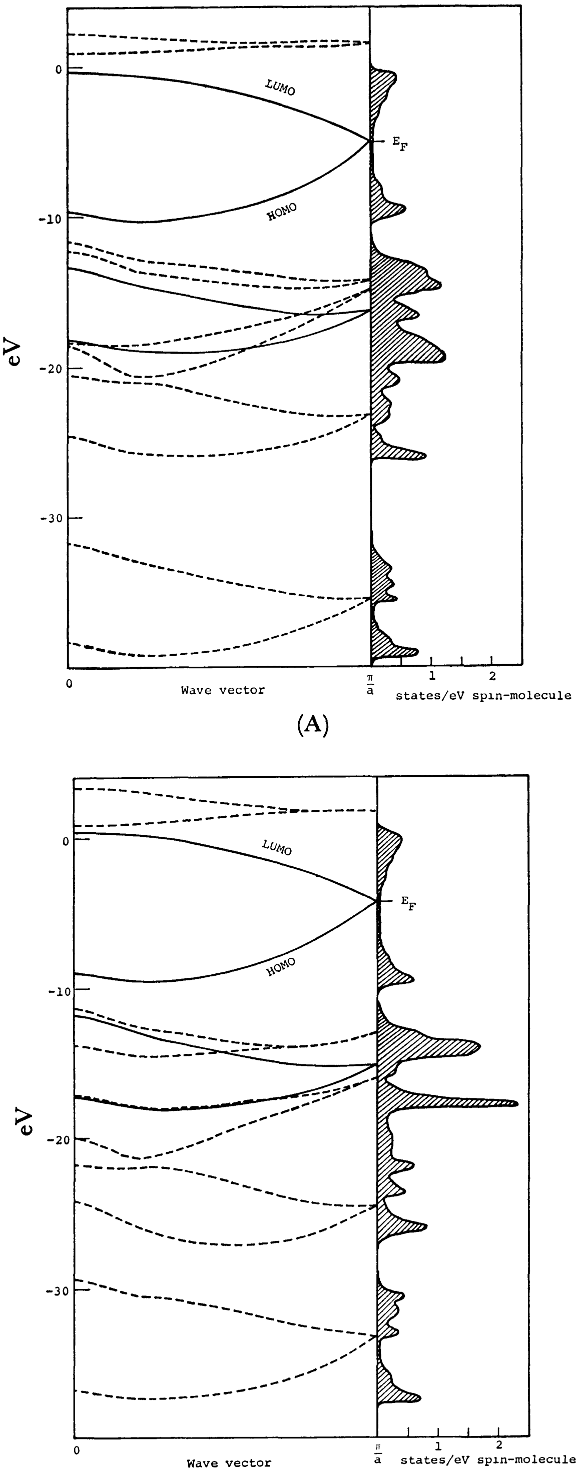
a) Ref. 8. For this structure, p_z, d_{xz}, d_{yz} and d_{z^2} AOs are the components of π orbitals. b) The total energy of $(SN)_2$ or $(SCH)_2$ molecule with the same configuration of the unit cell in $(SN)_x$ or $(SCH)_x$, respectively. c) The total energy of the most stable configuration (square form) of $(SN)_2$ molecule (Ref. 10). d) The value calculated by us on the same basis for the Pennsylvania structure.

also degenerate there. At such points, it is in principle unreasonable to describe the system with a single Slater determinant. Thus we extrapolated the density matrix elements at $K=\pm 9\pi/10a$ and $\pm\pi/10a$ to obtain those at $K=\pm\pi/a$ and 0, respectively. The values of overlap integrals between the central unit cell and the N-th nearest neighboring cell rapidly decrease to 0 where N=3—4 (9—13.5 Å from the central unit cell). But as those of electron repulsion (Coulomb) integrals slowly decrease, we consider them as far as the 7-th nearest neighbors (≈31 Å from the central unit cell).

Results and Discussion

The calculated results of AO densities, atomic net charges and the total energies per unit cell are shown in Table 1 along those of the Lyon structure of $(SN)_x$. As we set the direction of the polymer chain along the z-axis and the polymer plane perpendicular to the x-axis, the π orbitals are of $2p_x$, $3p_x$, $3d_{xy}$, and $3d_{xz}$ AOs. Both of $(SN)_2$ and $(SCH)_2$ units have six π electrons, supplied two π electrons from the sulfur atom and one from the nitrogen or the carbon atom. In $(SN)_x$ calculated here, the densities of $3p_x$ and $2p_x$ AOs on S and N are 1.407 and 1.218, respectively, and the contribution from $3d_{xy}$ and $3d_{xz}$ AOs is totally 0.375, the magnitude of which is not negligible. The atomic net charge on S is +0.231, and it is somewhat larger than that estimated for the Lyon structure, +0.186,[8] but somewhat less than that estimated by XPS method, +0.30—0.42.[7] In $(SCH)_x$, although the π electron densities on S and C are not so different from those on S and N in $(SN)_x$, the atomic net charge on S is +0.087 which is by far less than that in $(SN)_x$. This would be direct reflection of the electronegativity of each atom, namely S<C<N in order. It is also interesting that the atomic net charge on H is very close to that on S. It is clearly shown, from the difference in the total energies of a unit cell and isolated $(SN)_2$ molecules, that the polymeric state is more stable than the isolated molecules. Moreover, the comparison of the total energies per unit cell of the two structures of $(SN)_x$ definitely shows that the Pennsylvania structure is favorable. For $(SCH)_x$, it is similarly predicted that the polymeric state is stable in comparison with the isolated $(SCH)_2$ molecule.

The energy bands and the state densities of the polymers are shown in Figs. 2(A) and (B). The curves of the state densities are obtained with the Brust's method[17] summing over 300 points sampled in the Brillouin zone for each energy band. The valence bands consist of three π bands and eight σ bands, and the HOMO and the LUMO bands are of π MOs mainly composed of the sulfur $3p_x$ AO in both $(SN)_x$ and $(SCH)_x$. These energy bands of $(SN)_x$ and $(SCH)_x$ are seen to be of rather similar shape and the Fermi energies (E_F) are obtained as −4.996 and −4.340 eV, respectively. E_F of the Lyon structure of $(SN)_x$ has been reported to be −5.714 eV.[8] The shape of the state density of $(SN)_x$ agrees qualitatively with those obtained previously by ESCA spectroscopy.[7,18] The state density at E_F ($D(E_F)$) is small but finite for $(SN)_x$, namely, 0.04 states/eV spin-molecule, which shows the metallic nature of $(SN)_x$. Experimental value of $D(E_F)$ is 0.12—0.18 states/eV spin-molecule[18,19] which agrees quantitatively with our result but is somewhat larger, showing perhaps the reflection of the actual three-dimensional structure of $(SN)_x$ crystal. For $(SCH)_x$, the shape of the state density again resembles that of $(SN)_x$ but the peaks are more sharpened than in $(SN)_x$, and $D(E_F)$ is 0.06 states/eV spin-molecule. This value encourages us that $(SCH)_x$ may become also a metallic conductor if it should be successfully synthesized, and unless any interference such as Peierls transition



(A)

(B)

Fig. 2. The band structures and the state densities of (A) $(SN)_x$ and (B) $(SCH)_x$. Dotted lines and solid ones indicate σ bands and π bands, respectively. The upper several vacant MO bands and the state densities of those which are upper than the LUMO bands are not essential and omitted here.

should occur to break down the metallic state of $(SCH)_x$.

The E_{AB} analyses in the scheme of the CNDO/2 method are shown in Fig. 3 for $(SN)_x$ and $(SCH)_x$. It is shown that N_1–S_4 in $(SN)_x$ and S_1–C_6 in $(SCH)_x$ are both attractive. Moreover, it should be noticed that, both in $(SN)_x$ and in $(SCH)_x$, S_2–S_4 and S_1–S_4 are considerably attractive, while N_1–N_3 and C_3–C_6 are weakly repulsive, and hence the skeleton of each unit cell is held rather tightly. This would cause interesting effects to the force constant of the lattice displacement and to the Debye frequency of the system.

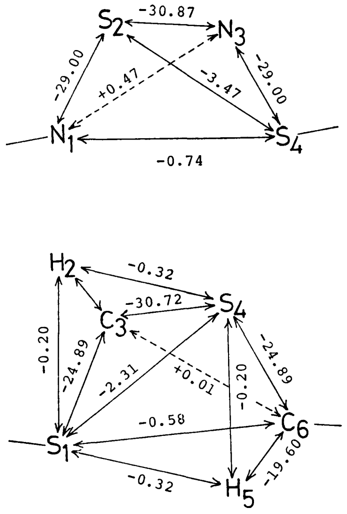


Fig. 3. The E_{AB} analyses for the representative unit cells of $(SN)_x$ and $(SCH)_x$. The energies are shown in eV. Dotted lines and solid ones indicate the repulsive and attractive interactions, respectively.

It is also noticed that much attention should be paid to the description of the system at $K=\pm\pi/a$, since there occurs a degeneracy of the HOMO and the LUMO bands. In order to overcome such a situation, some appropriate linear combination of the Slater determinants (Configuration Interaction) should be adopted.

The possibility of the interaction between two $(SN)_x$ chains or the highly anisotropic two- or three-dimensionality of $(SN)_x$ crystal has also been pointed out from some experimental aspects.[10,20] The SCF-tight-binding calculation including two chains is desirable.

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