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A Through Space/Bond Interaction Analysis on the Shape of Band Structure of Polynitrilomethylidyne

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The concept of the through space/bond interaction presented by Hoffmann *et al.* was extended to study electronic states of polymers. The band shape of lone pair orbitals was investigated by truncating converged Fock matrices and overlap integrals except for the terms corresponding to the through bond and particular through space interactions. This method was used by applying the *ab initio* tight-binding crystal orbital method to three isomers of one-dimensional polynitrilomethylidyne, for which the dependences of the lone pair orbital energy on the wave number vector differ significantly from one another. The band shape of the lone pair orbital is related intimately to the interaction with H atoms. The effect of each through space interaction on the band shape of the lone pair orbital may be reasonably interpreted in terms of the symmetry of crystal orbitals. This method seems expedient for analyzing qualitatively lone pair bands of various polymers at the *ab initio* level.

The concept of the through space/bond interaction introduced by Hoffmann *et al.* in 1968 has made a great contribution to the evaluation of the size of interaction between lone pair orbitals.[1] The through bond interaction can be quantitatively analyzed in more detail by using localized molecular orbitals transformed from canonical molecular orbitals. In the present article, an application of this through space/bond concept to one-dimensional polymer systems by using atomic orbitals was attempted in expectation of characterizing electronic states of various polymers.

In recent years a number of theoretical studies on conjugated organic polymers have been reported. We chose polynitrilomethylidyne, which possesses conjugated carbon–nitrogen double bonds, as a model polymer system for test calculation on the through space/bond interaction. This polymer has recently been synthesized, and it was found that the conductivity $\sigma_{300\text{K}}$ was up to $10^{-10}\ \Omega^{-1}\text{cm}^{-1}$ in spite of the possession of an even number of electrons in the unit cell.[2,3] For this reason polynitrilomethylidyne has been the object of several theoretical studies. Polynitrilomethylidyne is composed of trans-zigzag, trans-cisoid, and cis-transoid forms as shown in Fig. 1. For the trans-zigzag form, Karpfen[4,5] carried out an optimization of the geometry at the Hartree-Fock *ab initio* double zeta level by assuming that the unit cell of an infinite polymer consists of a single HCN molecule. Furthermore, the force constant, band structure, and density of state were investigated in comparison with those for polyacetylene in the literature.[6] Kertesz and co-workers[7,8] applied the restricted and unrestricted Hartree-Fock methods to studying the alternating and nonalternating structures of the trans-zigzag $(\text{-HCN-})_x$ linear chains. Bredas *et al.*[9,10] calculated the ionization potential, band width, and band gap for the trans-zigzag polynitrilomethylidyne by using the valence effective Hamiltonian technique. For the hydrogen-bonded hydrogen cyanide polymer chain, *ab initio* studies based on crystallographic data[11,12] were previously reported in comparison with HCN molecules or their aggregates.[13,14] On the other hand, the trans-cisoid and cis-transoid forms have only rarely been studied in detail from the theoretical point of view.

In this study, *ab initio* calculations were performed on the three isomers of polynitrilomethylidyne, and by using the matrix elements obtained the through space/bond method was applied to analyzing the lone pair bands. The purpose of this study was to investigate the applicability of this method by examining the influence of the interaction between atomic orbitals on the shape of lone pair bands.

Method

The *ab initio* crystal orbital method used in this study is based on the general SCF tight-binding LCAO formalism[15] corresponding essentially to Roothaan's Hartree-Fock equation for molecules,[16] taking into account all neighbor interactions and overlap integrals. The outline of this theory is described below. A delocalized wave function of a single electron in the periodic potential of a one-dimensional crystal is represented as a linear combination of Bloch basis orbitals $\phi_i^k(r)$, which are written as periodic combinations of n atomic orbitals χ_r:

$$\phi_i^k(r_1) = (2N+1)^{-1/2}\sum_{m=-N}^{+N}\sum_{r=1}^{n}\exp(\mathbf{i}kR_m)C_{ir}(k)\chi_r(r_1-R_m), \quad (1)$$

where k denotes a wave number vector in the first Brillouin zone, i an energy band, and $\mathbf{i}$ the imaginary number or the square root of -1. The term $\chi_r(r_1-R_m)$ stands for an atomic orbital localized in the m-th cell at $R_m(m=0, \pm1, \pm2, \cdots\cdots, \pm N)$, and $2N+1$ is the number of elementary cells. Applying the well known non-relativistic Hamiltonian

$$H = \sum_{\mu}\left\{-\frac{1}{2}\Delta_{\mu} + V(\mu)\right\} + \sum_{\mu>\nu}\frac{1}{r_{\mu\nu}} \quad (2)$$

to the antisymmetrized product of the one-electronic wave function Eq. 1 and using the orthonormality condition

$$\langle\phi_i^k(r_1)|\phi_j^k(r_1)\rangle = \delta_{ij}, \quad (3)$$

we obtain the total electronic energy as

$$E = 2\sum_{i}^{\mathrm{occ}} H_{ii} + \sum_{i}^{\mathrm{occ}}\sum_{j}^{\mathrm{occ}} (2J_{ij} - K_{ij}) \tag{4}$$

where

$$H_{ij} = \int \phi_i(1)\left\{-\frac{1}{2}\Delta_1 + V(1)\right\}\phi_j(1)\,\mathrm{d}\tau_1,$$

$$J_{ij} = \iint \phi_i(1)\,\phi_j(2)\frac{1}{r_{ij}}\phi_i(1)\phi_j(2)\mathrm{d}\tau_1\mathrm{d}\tau_2,$$

$$K_{ij} = \iint \phi_i(1)\,\phi_j(2)\frac{1}{r_{ij}}\phi_j(1)\phi_i(2)\mathrm{d}\tau_1\mathrm{d}\tau_2,$$

Substituting the crystal orbital Eq. 1 into Eq. 3 and using the periodic boundary condition, we obtain the corresponding total electronic energy per unit cell as

$$\begin{aligned} E = {} & 2\sum_{i}^{\mathrm{occ}} \sum_{k=0}^{2\pi} \sum_{r} \sum_{s} C_{ir}^{*}(k) C_{is}(k) \sum_{m=-M}^{+M} \exp(\mathbf{i}kR_m) I_{rs}^{0m}(R_m) \\ & + \sum_{i}^{\mathrm{occ}} \sum_{k=0}^{2\pi} \sum_{m}\sum_{h}\sum_{l}\sum_{r}\sum_{s}\sum_{t}\sum_{u} P_{tu}^{hl} C_{ir}^{*}(k) C_{is}(k) \exp(\mathbf{i}kR_m) \\ & \times \left\{ 2\left\langle \begin{matrix}0m\\ rs\end{matrix} \middle| \begin{matrix}hl\\ tu\end{matrix} \right\rangle - \left\langle \begin{matrix}0h\\ rt\end{matrix} \middle| \begin{matrix}ml\\ su\end{matrix} \right\rangle \right\}, \end{aligned} \tag{5}$$

where M denotes the number of cells included in the summation, and

$$I_{rs}^{0m}(R_m) = \langle \chi_r(r_1) | h(1) | \chi_s(r_1 - R_m) \rangle,$$

$$P_{tu}^{hl} = (2N+1)^{-1} \sum_{k'=0}^{2\pi} \sum_{j=1}^{\mathrm{occ}} \exp\{\mathbf{i}k'(R_l - R_h)\} C_{jt}^{*}(k') C_{ju}(k'),$$

$$\left\langle \begin{matrix}0m\\ rs\end{matrix} \middle| \begin{matrix}hl\\ tu\end{matrix} \right\rangle = \langle \chi_r(r_1)\chi_s(r_1 - R_m) | r_{12}^{-1} | \chi_t(r_2 - R_h)\chi_u(r_2 - R_l) \rangle,$$

These last three equations correspond to the one-electron core integral, the density matrix, and the two-electron integral, respectively. Symbols r, s, t, and u denote the atomic orbitals in the elementary cells characterized by symbols 0, m, h, and l, respectively. Putting the overlap integral between the r-th atomic orbital in the central cell and the s-th atomic orbital in the m-th cell as

$$S_{rs}^{0m}(R_m) = \langle \chi_r(r_1) | \chi_s(r_1 - R_m) \rangle \tag{6}$$

and applying the Ritz variation method to the Eq. 5, we can obtain the eigenvalue problem

$$\sum_{s} \sum_{m=-M}^{+M} \exp(\mathbf{i}kR_m)[F_{rs}^{0m}(R_m) - S_{rs}^{0m}(R_m)E_i(k)]C_{is}(k) = 0, \quad (k=0, \cdots, 2\pi) \tag{7}$$

where F_{rs}^{0m} is the Fock matrix element between the r-th atomic orbital in the central segment and the s-th atomic orbital in the m-th cell and is given by

$$\begin{aligned} F_{rs}^{0m}(R_m) = {} & I_{rs}^{0m}(R_m) \\ & + \sum_{h}\sum_{l}\sum_{t}\sum_{u} P_{tu}^{hl} \left\{ 2\left\langle \begin{matrix}0m\\ rs\end{matrix} \middle| \begin{matrix}hl\\ tu\end{matrix} \right\rangle - \left\langle \begin{matrix}0h\\ rt\end{matrix} \middle| \begin{matrix}ml\\ su\end{matrix} \right\rangle \right\}. \end{aligned} \tag{8}$$

If the expression for the Fock matrix element between Bloch orbitals $F_{rs}(k)$ and that for the corresponding overlap integral $S_{rs}(k)$ are defined as

$$F_{rs}(k) = \sum_{m=-M}^{+M} \exp(\mathbf{i}kR_m) F_{rs}^{0m}(R_m), \tag{9}$$

$$S_{rs}(k) = \sum_{m=-M}^{+M} \exp(\mathbf{i}kR_m) S_{rs}^{0m}(R_m), \tag{10}$$

then the eigenvalue problem for a given value of k in the first Brillouin zone is obtained as

$$\sum_{s} F_{rs}(k) C_{is}(k) = \sum_{s} S_{rs}(k) C_{is}(k) E_i(k). \tag{11}$$

As a result the secular equation to be solved is given by

$$|F_{rs}(k) - S_{rs}(k)E_i(k)| = 0. \tag{12}$$

Based on this theory, the Polymer Gaussian 74 program has been extensively developed by Suhai[6] within the Hartree Fock scheme. *Ab initio* calculations were performed on three typical isomers of the polynitrilomethylidyne one-dimensional model polymer by using this program with an STO-3G basis set. The k-points in half the Brillouin zone were used, and the convergence criterion of 10^{-6} for the difference of density matrix elements was adopted. Twice the magnitude of the lattice vector was taken as a translational vector corresponding to the unit cell shown in Fig. 1, and the contribution up to the seventh neighbor interaction in core resonance integrals and two- electron integrals was taken into consideration. The influence of lattice sum truncation on computed total energy and energy bands for the three forms of polynitrilomethylidyne were investigated. The geometries used here are the same as those described in Refs. 17 and 18 for the CNDO/2 method.

The natural development of this study was the introduction of the through bond/space concept into polymer systems. Analysis of band shapes must be possible by neglecting Fock matrix elements and overlap integrals between particular

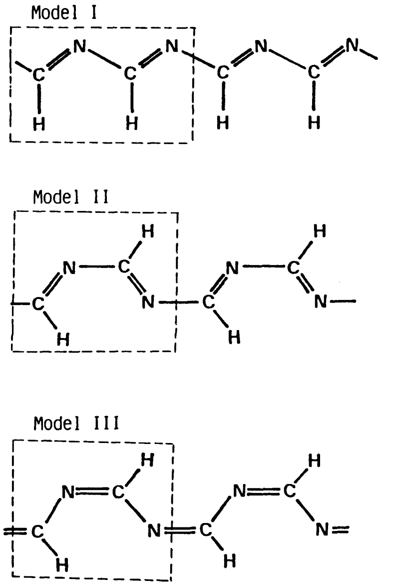

Fig. 1. Structures of the isomers of polynitrilomethylidyne: trans-zigzag (Model I), trans-cisoid (Model II) and cis-transoid (Model-III). The unit cells are surrounded with broken lines.

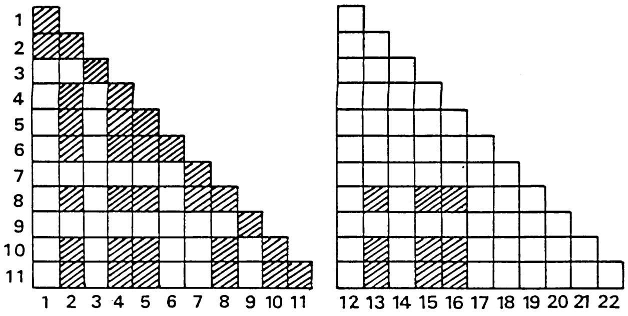

Fig. 2. Through bond interaction elements: (a) terms within a single HCN unit. (b) terms between nearest neighboring two single HCN units. 1—5: 1s, 2s, $2p_x$, $2p_y$, $2p_z$ orbitals on C atom; 6: 1s orbital on H atom; 7—11: 1s, 2s, $2p_x$, $2p_y$, $2p_z$ orbitals on N atom; 12—16: 1s, 2s, $2p_x$, $2p_y$, $2p_z$ orbitals on the neighboring C atom; 17: 1s orbital on the neighboring H atom; 18—22: 1s, 2s, $2p_x$, $2p_y$, $2p_z$ orbitals on the neighboring N atom. This polymer is on the y—z plane.

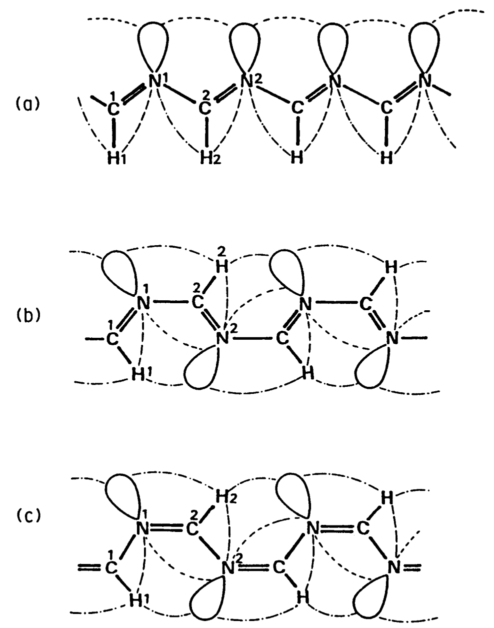

Fig. 3. The main through space components used in this analysis.
········ N1-N2 interaction, ——— N1-H1 and N2-H2 interaction, —·—·— N1-H2 and N2-H1 interaction.
(a) Model I, (b) Model II, (c) Model III.

atomic orbitals. Then all Fock matrix elements and overlap integrals were classified into two kinds of interaction patterns. One type is those terms relating to the through bond interactions which include the Fock matrices given by Eq. 9 and overlap integrals given by Eq. 10 for diagonal elements and those between the 1s and 2s orbitals belonging to the same atom and between valence orbitals belonging to the nearest neighboring atoms. Here, valence orbitals mean the 2s, $2p_x$, $2p_y$, and $2p_z$ orbitals on the C and N atoms and the 1s orbitals on the H atoms. The matrix elements of the through bond interaction in the secular equation Eq. 12 for polynitrilomethylidyne are shown in Fig. 2(a) for the terms within a single HCN unit and in Fig. 2(b) for the terms between two single nearest neighbor HCN units. These elements were included for all cases of analyses. The other type is the through space interactions which include the terms except those for the through bond interaction, that is, those between particular valence orbitals belonging to different atoms. In this study three kinds of through space interactions shown in Fig. 3 were selected for the analysis of the lone pair bands. The procedure for the actual calculation was as follows:

1. The Fock matrix elements and the overlap integrals converged by usual *ab initio* calculations were stored.
2. Of the elements obtained in step 1, the through bond elements shown in Figs. 2(a) and (b), and only significant elements in the through space interactions were explicitly taken into account; the other elements were left out.
3. By using the new matrix elements retained in step 2, the eigenvalue problem given by Eq. 11 for each wave number vector was solved only once without further iterations.

The Gaussian 74 program was modified for the abovementioned procedure. The relationship between band shapes and crystal orbitals for each through space interaction can be investigated by using the eigenvectors and energies obtained in step 3. The change in energy bands caused by increasing through space components between selected pairs of atomic orbitals, revealed a trend quantitatively consistent to the full interaction. In this process, the most significant through space interaction was found by comparing changes of band shapes.

Results and Discussion

The finite neighbor approximation is a difficult problem in the evaluation of multi-center integrals because even Fock matrix elements obtained with wrong cutoff conditions give artificially stable energy states. Suhai has reported that total energies are strongly dependent upon the number of neighbors included, and that the sphere of elementary cells within which Fock matrix elements have to be calculated is determined only by the magnitude of exchange integrals. His study for polyacetylene demonstrated that

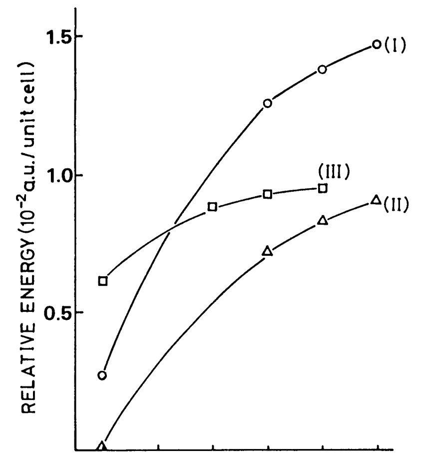

Fig. 4. Relative total energy per $-\!(\text{HCN})\!-_2$ unit as function of the number (M) of interacting $-\!(\text{HCN})\!-_2$ neighbors in three models of polynitrilomethylidyne Model I, Model II, and Model III.

limiting converged energies were obtained finally by taking into consideration up to the 28th neighboring C_2H_2 unit. In order to obtain some insight into convergency properties of the three forms of polynitrilomethylidyne, *ab initio* calculations were carried out for each case which includes the lattice summation up to each of the third to eighth neighbor interactions. Figure 4 shows that the third neighbor approximation is insufficient to obtain converged energy values. The total energy difference converges to a certain extent with up to eight neighbor lattice summations, but the effect of lattice truncation does not completely disappear. We did not determine for polynitrilomethylidyne how far interactions in the two-electron integrals should be taken into consideration to reach the correct limiting value, because it was not the purpose of this study.

The band structures and densities of state obtained by

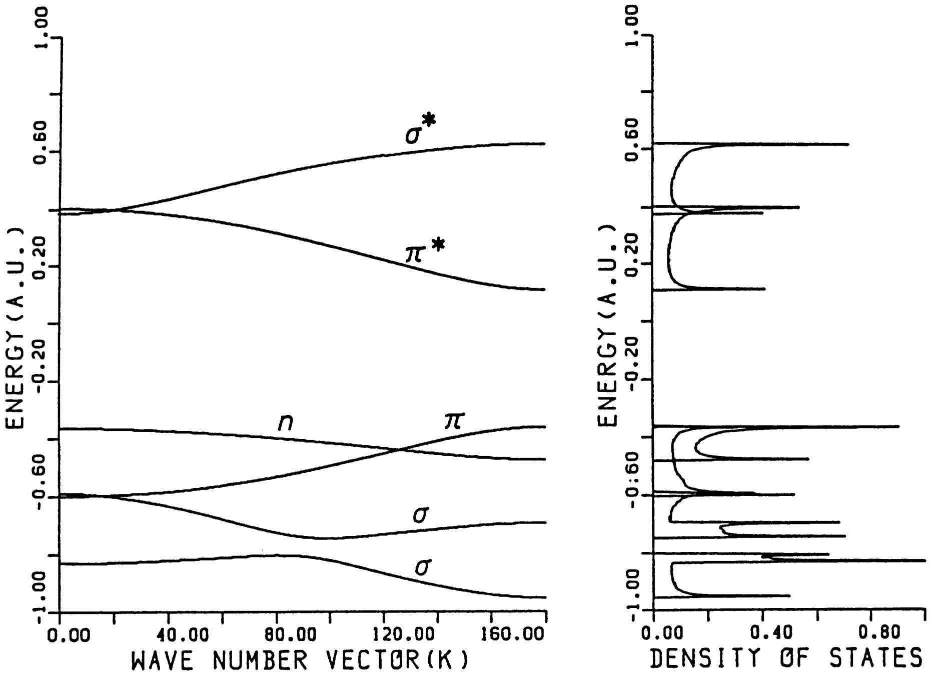

Fig. 5. Band structure and density of states of trans-zigzag polynitrilomethylidyne.

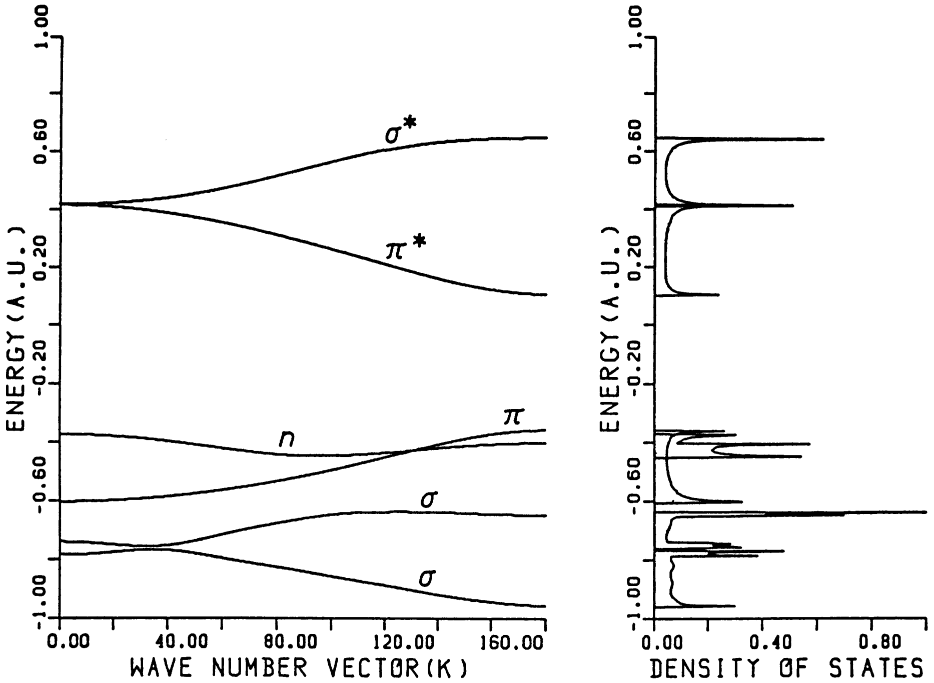

Fig. 6. Band structure and density of states of trans-cisoid polynitrilomethylidyne.

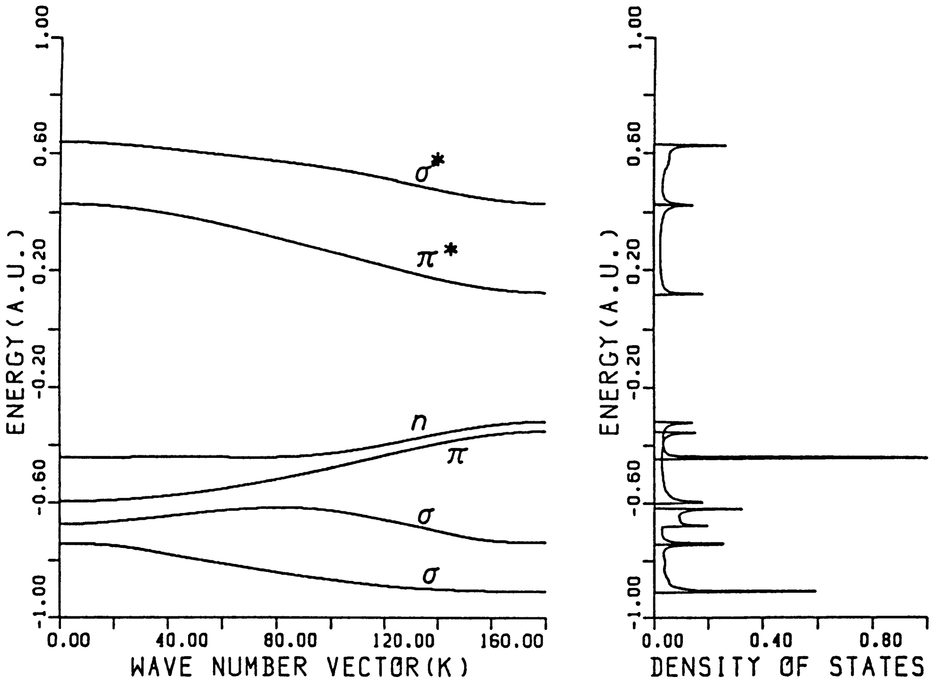

Fig. 7. Band structure and density of states of cis-transoid polynitrilomethylidyne.

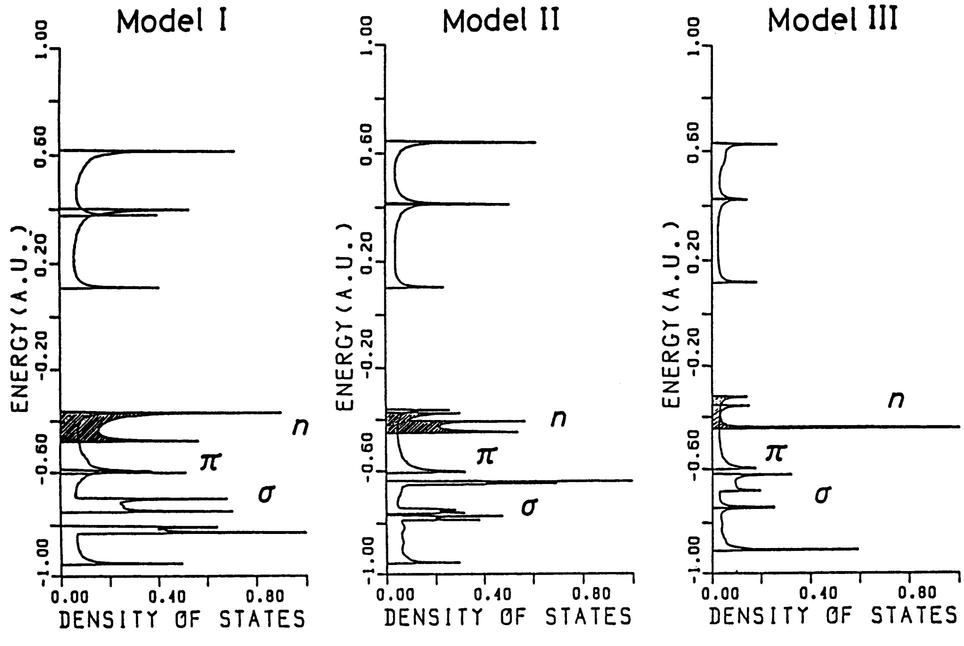

Fig. 8. Density of states for three models of polynitrilomethylidyne.

including up to the seventh neighbors are shown in Figs. 5—7 for the three forms of polynitrilomethylidyne. These polymers are insulators because the band gaps between the valence and conduction bands are as much as 12.0—12.5 eV. The energy bands obtained by these *ab initio* calculations with the STO-3G basis set indicate that the bands are correspondingly similar for the three isomers, but that the lone pair bands on the N atoms differ from one another significantly. In particular, it is noteworthy that there are three peaks in the density of state for the lone pair band of the trans-cisoid form in contrast to the other two forms, as can be seen in Fig. 8. The magnitudes of the energies for all the wave number vectors at the seventh neighbor level are larger for the three forms by about 0.01 au than those at the third neighbor level, but no effect on the band shape is caused by the increase in number of included neighbors. Therefore, the effect of the more distant neighbors on the interaction pattern between orbitals may be neglected without leading to serious errors. So the lone pair bands of the three forms were analyzed by the through space/bond method based on the matrix

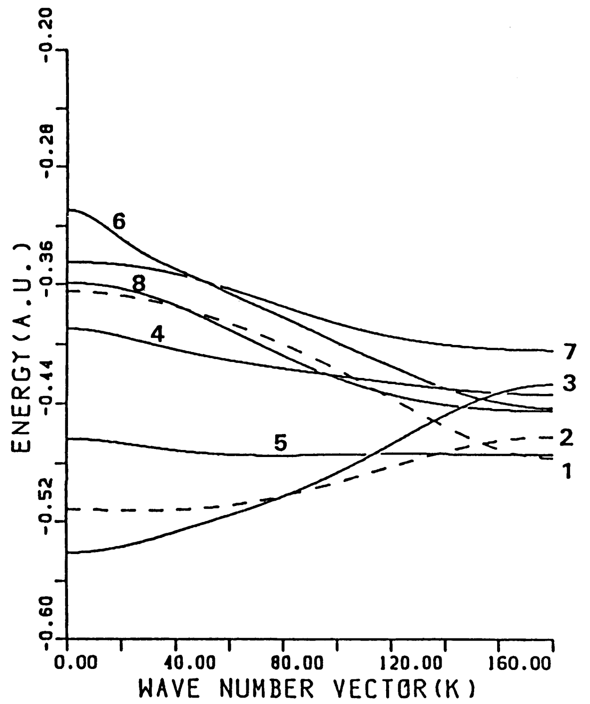

Fig. 9. The change in energy band of the lone pair orbital by analysis of the through space/bond method for Model I. 1. Full interaction, 2. Through bond interaction. The interactions 3—8 are shown added to 2. 3. N1-N2 interaction, 4. N1-H1 and N2-H2 interaction, 5. N1-H2 and N2-H1 interaction, 6. 4+5, 7. 3+4+5 and C(valence orbitals)-N(1s orbital).

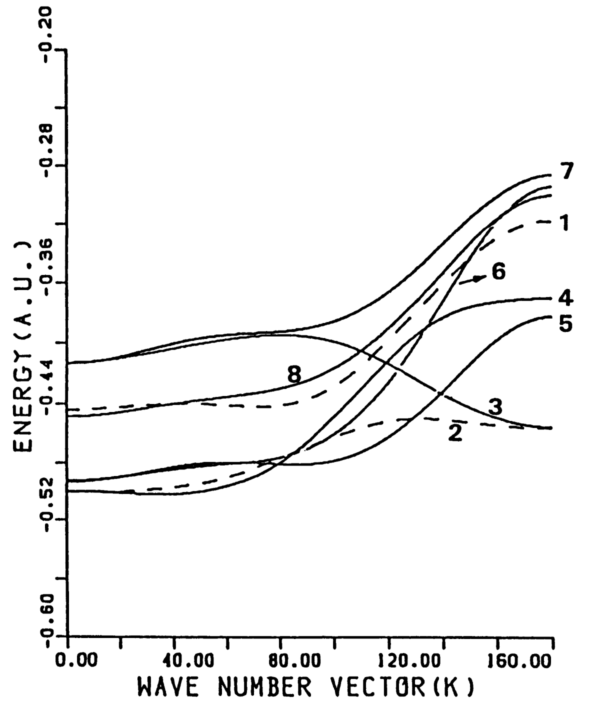

Fig. 11. The change in energy band of the lone pair orbital by analysis of the through space/bond method for Model III. The notations used in this figure are the same as those in Fig. 9.

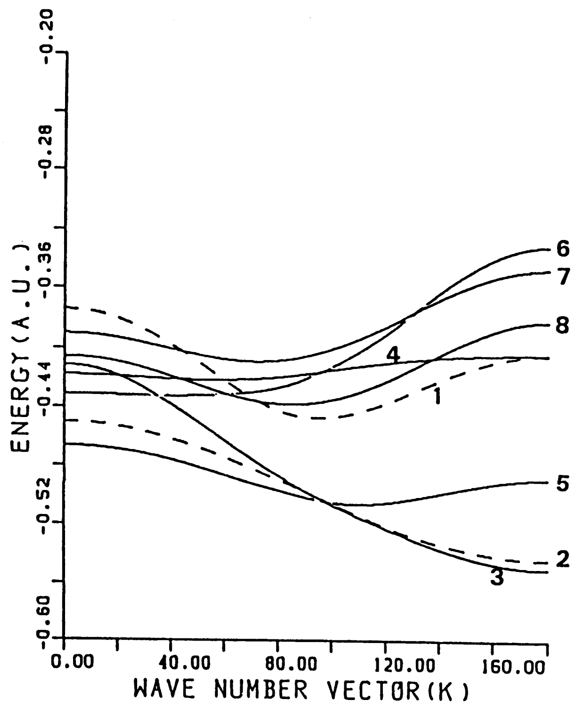

Fig. 10. The change in energy band of the lone pair orbital by analysis of the through space/bond method for Model II. The notations used in this figure are the same as those in Fig. 9.

elements obtained by including up to the third neighbors, in order to clarify which interaction between the atomic orbitals is most important.

The lone pair bands obtained by this through space/bond analysis are shown in Figs. 9—11 for trans-zigzag, trans-cisoid, and cis-transoid forms, respectively. The broken curve 1 refers to the full interaction including all the interactions between atomic orbitals, and the broken curve 2 to the pure through bond interaction including only the matrix elements between valence orbitals on two directly bonded atoms as shown in Fig. 2. We chose the six interactions denoted by 3—8 in Figs. 9—11 as the through space interactions to be added to the pure through bond interaction. In interactions 3—7 only the interactions between valence orbitals are included. The effect of each through space interaction on the lone pair band is discussed below for the three forms of polynitrilomethylidyne in terms of the symmetry or the phase of crystal orbitals. In crystal orbitals the range k=0°—90° belongs to the symmetric band within a unit cell and the range k=90°—180° to the antisymmetric band. The crystal orbitals at k=0° and 180° are schematically shown in Fig. 12. Furthermore, the crystal orbitals at k=0° and 180° are symmetric with respect to those of the nearest neighboring unit cells. Therefore, the crystal orbitals at k=0° are symmetric within a unit cell and symmetric to the nearest neighboring unit cells, whereas the crystal orbitals at k=180° are antisymmetric within a unit cell and symmetric to the nearest neighboring unit cells.

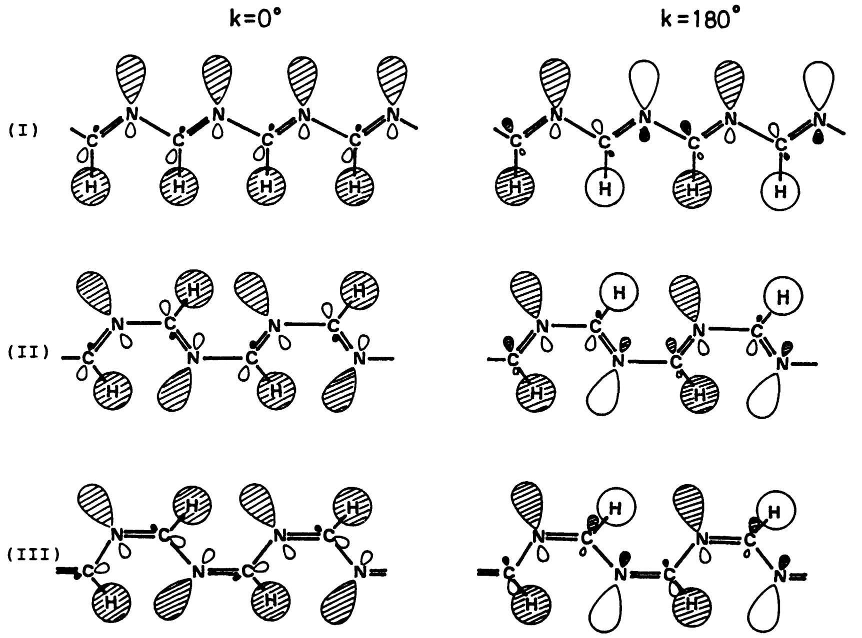

Fig. 12. Schematic representation of the magnitude of the coefficients of the atomic orbitals in the crystal orbitals in the through bond interaction for the three models of polynitrilomethylidine. Shaded areas represent positive lobes; unshaded negative.

Model I. When interaction 3 between orbitals on the neighboring N atoms (see Fig. 3) was added to the through bond interaction, the energy of the MO was lowered by 0.03 au at k=0° and raised by 0.04 au at k=180°. As shown in the schematic orbitals (Fig. 12(I)), the lone pair orbitals belonging to N1 and N2 are symmetric at k=0° and antisymmetric at k=180° within a unit cell and symmetric with respect to the nearest neighboring unit cells at both the k-points; that is, all the overlap integrals between the nearest neighboring lone pair orbitals are positive at k=0° and negative at k=180°. Therefore, it should be expected that the MO is stabilized at k=0° and destabilized at k=180° due to interaction 3, since the positive overlap implies bonding and the negative one anti-bonding. By interaction 4 between the lone pair orbital on N1 and the 1s orbital on H1 as well as on N2 and H2 (see Figs. 3 and 12), the MO is raised by 0.12 au in energy at k=0° and by 0.03 au at k=180° relative to the pure through bond interaction 2. It seems that this change relates to the antibonding properties between the orbitals on N1 and H1 or N2 and H2, because the enlarged lone pair orbital on the N atom and the 1s orbital on the H atom are out-of-phase within a single HCN molecule at all the k-points. By interaction 5 between the lone pair orbital on N1 and the 1s orbital on H2 or on N2 and H1, the MO is raised by 0.05 au in energy at k=0° and lowered by 0.015 au at k=180°. This can be considered to be caused by the negative overlap between the lone pair orbital on N1 and the 1s orbital on H2 at k=0° and the positive overlap at k=180° in all the unit cells. The greater destabilization in interaction 4 than that in interaction 5 at k=0° may be due to the shorter distance in interaction 4 between the N and H atoms. By interaction 6 which consists of interactions 4 and 5, the band shape is made roughly similar to that for the full interaction 1. The additivity rule holds approximately for the through bond interaction because the energy gain in interaction 6 relative to the through bond interaction 2 corresponds nearly to the sum of the increases from interactions 4 and 5 at all the k-points. By interaction 7 which is equal to the interaction 6 having the interaction between the lone pair orbitals on the neighboring N atoms added, the MO is lowered by 0.03 au in energy at k=0° and raised by 0.04 au at k=180°. Interaction 6 is to interaction 7 what the pure through bond interaction 2 is to interaction 3. Finally by interaction 8 which is equal to interaction 7 having the interaction between the 1s orbital on the N atom and the valence orbitals (2s, $2p_x$, $2p_y$, and $2p_z$) on the C atom added, the band shape is in approximate agreement with the full interaction 1 except near k=180°. It was found that the effect of the interaction between the 1s orbital of N and the valence orbitals of C should not be neglected since the lone pair band is stabilized to some extent by this interaction. In conclusion, it was ascertained that interaction 6 between the lone pair orbital and the H atoms belonging to both neighboring C atoms dominates the through space interaction.

Model II. In this structure which is planar and possesses a screw axis symmetry in a unit cell, the interaction between the lone pair orbital and the 1s orbital on the H atom would be expected to be the main through space interaction, judging from the positions of the atoms around the lone pair orbital. Similar reasoning as has been developed for the trans-zigzag form can be applied to the trans-cisoid form. By interaction 3, the MO is raised by 0.04 au in energy at $k=0°$ and is lowered by 0.01 au at $k=180°$ relative to the through bond interaction 2. As shown in the schematic orbitals (Fig. 12(II)), the overlap between the neighboring lone pair orbitals possesses antibonding properties at $k=0°$ and bonding properties at $k=180°$ over all the unit cells, since the enlarged lone pair orbitals within a unit cell are out-of-phase at $k=0°$—$90°$ and in-phase at $k=90°$—$180°$. This is probably the reason for the destabilization in energy at $k=0°$ and the stabilization at $k=180°$. By interaction 4 (see Figs. 3 and 10), the MO is raised by 0.03 au in energy at $k=0°$ and by 0.14 au energy at $k=180°$. As in the trans-zigzag form, this behavior is considered to relate to the antibonding properties between the lone pair orbital on N1 and the 1 s orbital on H1 or on N2 and H2, because the lone pair orbital and the 1 s orbital on the H atom are out-of-phase within a single HCN molecule. By interaction 5, the energy level is lowered by 0.1 or 0.2 au in energy at $k=0°$ and raised by 0.05 au at $k=180°$. This may be due to the positive overlap at $k=0°$ and the negative overlap at $k=180°$ between the 1 s orbital on H1 and the lone pair orbital on N2, as can be seen from the phase of the MO. Because of this through space interaction, the band shape becomes closely similar to that for the full interaction 1, aside from the values of energy. Interaction 6, equal to the interaction 5 with interaction 4 added, has the same effect as the through bond interaction 2 has on interaction 4, that is, the MO is raised by 0.04 au in energy at $k=0°$ and by 0.16 au at $k=180°$ By interaction 7, for which interaction 3 between the nearest neighboring lone pair orbitals has been added to interaction 6, the MO is raised by 0.04 au in energy at $k=0°$ and lowered by 0.02 au at $k=180°$. As in the trans-zigzag form, the additivity rule approximately holds for interactions 3 and 6 in the through bond interaction 7. By interaction 8, the band shape is allowed to have a more consistent trend toward that for the full interaction 1. It was found that the 1 s orbital on N has a considerable contribution to the stabilization of the lone pair band in a similar manner as it has in the trans-zigzag form. The result that interaction 5 is the most important through space interaction in determining the band shape of the lone pair orbital in this trans-cisoid form, may be expected from the structure of the polymer.

Model III. By interaction 3, the energy level relative to that for interaction 2 is raised by as much as 0.09 au at $k=0°$, in contrast with little change at $k=180°$. As shown in the schematic orbitals (Fig. 12(III)), this behavior can be considered to be caused by the larger magnitude of the negative overlap at $k=0°$ than that of the positive overlap at $k=180°$ between the nearest neighboring lone pair orbitals. Otherwise, considering the shape of the wave function obtained, there may be a possibility that the difference in shape between the crystal orbitals on the C atoms is related to this behavior through a second order effect arising from this through space perturbation. By interaction 4, the MO is raised by 0.09 au at $k=180°$ due to the expected large negative overlap (see Figs. 3 and 12). On the other hand, no effect can be seen at $k=0°$, in contrast with the case of the trans-cisoid form. By interaction 5, the MO is raised by 0.01 au at $k=0°$ and by 0.075 au at $k=180°$. The destabilization at $k=180°$ can be considered to be caused by the large negative overlap, but this explanation seems inapplicable at $k=0°$. The band shape at all the k-points closely resembles that for the full interaction as with the trans-cisoid form, aside from the magnitude of energy. By interaction 6, which is equal to interaction 5 having interaction 4 added, the MO is raised by 0.09 au at $k=180°$ but not changed at $k=0°$. The additivity rule holds almost exactly since the energy gain in interaction 6 over the through bond interaction 2 corresponds to the sum of those in interactions 4 and 5 at all the k-points. By interaction 7, the MO is raised by 0.08 au at $k=0°$ and 0.01 au at $k=180°$ relative to that for interaction 6, and the additivity rule holds approximately. By interaction 8, the band shape is made still more similar to that for the full interaction as in models I and II. The result is that interaction 5 is the most important through space interaction as in the case of the trans-cisoid form. On the other hand, the energy level near $k=0°$ is hardly affected by the through space interaction between the lone pair orbitals and the 1 s orbitals on the H atoms, in contrast with the case of the trans-cisoid form. The differences between the trans-cisoid and cis-transoid forms with respect to the k-dependence of the lone pair band due to each through space interaction may result from the difference in the second order contribution of the through space perturbation. With respect to this point, more quantitative analysis is required for more detailed comparison.

Summary of the Results for Models I, II, and III. Although k-dependences of energy levels vary from model to model, they can reasonably be interpreted on the basis of the schematic orbitals shown in Fig. 12. For interaction 3, model I leads to a dependence different from those given by models II and III, in conformity with their differences in molecular structure. Of the various interactions adopted, the most important one for the determination of the curve shape is interaction 6 (composed of interactions 5 and 6) for model I and interaction 5 for models II and III. This consequence is in accord with the molecular structures of models I, II, and III. For all models I—III, interaction 8 gives curve shapes similar to those of the full interaction; that is, the interaction between the 1s orbital on the N atom and the valence orbitals on the C atom lowers the energy levels at all points of k, leading to the similar shapes. Finally, it should also be pointed out that the additivity rule for these interactions was found to hold approximately for all the three models.

Conclusion

In this paper we have developed a method for applying the through space/bond interaction to polymer systems at the *ab initio* level. As a result of applying this method to three isomers of polynitrilomethylidyne, it has been found that the interaction between the lone pair orbital and the H atoms bonded to both the neighboring C atoms governs the band shape of the lone pair orbital for the trans-zigzag form, and that the interaction between the lone pair orbital and the opposite H atoms belonging to the neighboring unit cell is most important for the trans-cisoid and cis-transoid forms. It is essentially desirable that energies of the through space interaction between pairs of localized crystal orbitals should be evaluated quantitatively. Therefore, this paper involves some obscurity in the definition of the through bond interaction because this analysis is based on atomic orbitals. However, qualitatively reasonable results on the relationship between the inter-orbital interaction pattern and the band shape have been obtained in spite of the omission of the troublesome transformation from atomic to localized orbitals. The results presented here have proved this method to be useful with the advantage of simplicity and convenience for rough estimation of the interaction between orbitals for various polymers possessing lone pair orbitals.

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