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Skeleton–side-group interaction in organopolysilane

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The skeleton–side-group interaction due to σ-π mixing in organopolysilane —$(\mathrm{Si}XY)_n$— where X and Y are methyl (Me) and phenyl (Φ) groups, has been theoretically investigated. The results are discussed on the basis of uv photoemission experiments. The σ-π interaction at the valence-band edge produces not only the delocalized σ states along the Si skeleton, but also the localized π states in the individual Φ side groups. On the other hand, the σ^*-π^* interaction at the conduction-band edge is inhibited owing to the orbital symmetry. This paper also presents the results of theoretical investigations on the influence of side-group substitution and of Φ–side-group rotation on the electron distribution along the Si skeleton.

I. INTRODUCTION

In chainlike polymers, there are several requirements if a skeleton–side-group interaction is to occur due to band mixing between the skeleton frontier states and the side-group electronic states. First, the frontier states [the highest occupied valence band (HOVB) and the lowest unoccupied conduction band (LUCB)] of the polymer chain must be determined by the skeleton atomic orbitals (AO's). Second, these frontier states must be energetically close to corresponding electronic states of the side groups. Of course, the AO's of the skeleton and side groups must be arranged in such a symmetry where the AO's are able to mix. When these requirements are satisfied, the skeleton frontier states of the polymer can be modified by the side-chain substituents.

A chainlike polymer with a Si skeleton—polysilane—is a type of semiconductor where an optical transition is directly allowed. Its band-edge states (HOVB and LUCB) are formed of skeleton Si AO's, and also extend along the skeleton.[1,2] Moreover, the energy position of this HOVB state is significantly higher than that of C-atom skeleton polymers,[3] and close enough to mix with the highest occupied molecular orbital (HOMO) levels of typical organic substituents (e.g., phenyl group). In fact, the possibility of skeleton–side-group interaction due to σ-π band mixing between skeleton σ electrons and side-group π electrons in phenylpolysilane has been pointed out.[4,10]

Recently, Loubriel and Zeigler[5] have experimentally shown this band mixing in organopolysilane high polymers. By comparing the photoelectron spectra between polyalkylsilane and polyarylsilane, they discussed the admixture of the wave functions of the side group and Si backbone at the valence-band (VB) edge state. In this work we calculate electronic structures for two typical organopolysilanes of dimethylpolysilane (DMePSi, alkylpolysilane) and methylphenylpolysilane (MeΦPSi, phenylpolysilane), and then investigate theoretically the mechanism of the skeleton–side-group interaction in such organopolysilanes. Results are discussed on the basis of ultraviolet photolectron spectroscopy (UPS) measurements. Theoretical investigations are also presented for the influence of the side-group substitution (alkylation or phenylation) and of phenyl (Φ) -group rotation on the electronic charge-density (CD) distribution along the Si skeleton.

II. THEORY

The method for the present band calculation was based on Slater and Koster's[6] (SK) (LCAO) approach, because of the covalency inherent to polysilane. In the LCAO method, the eigenfunction ϕ_α of the bound states of free atoms is used as the basis, and the wave function for an electron in solids can be expressed in terms of the LCAO Bloch sums as

$$\Psi_{\mathbf{k}}^{n}(\mathbf{r})=\sum_{\mathbf{R}_l} e^{i\mathbf{k}\cdot\mathbf{R}_l}\sum_{\alpha} C_{\alpha}^{n}(\mathbf{k})\phi_\alpha(\mathbf{r}-\mathbf{R}_l) \ . \tag{1}$$

The subscript n signifies the energy-band index, and $\mathbf{R}_l$ is the position vector of the lth unit cell. The symbol α labels the atomic eigenstate of quantum number (n,l,m) as well as indicating the atomic species in the unit cell. The valence-orbital approximation employs the valence eigenfunctions of Si $3s$, $3p_x$, $3p_y$, $3p_z$, C $2s$, $2p_x$, $2p_y$, $2p_z$, and H $1s$ AO's as basis. According to the conventional variation technique, the energy eigenvalue $E_{(\mathbf{k})}^{n}$ and eigenstates $C_\alpha^n(\mathbf{k})$ can be determined by the following secular equation:

$$\left| \varepsilon_\alpha \sum_{\mathbf{R}_l} e^{i\mathbf{k}\cdot\mathbf{R}_l}\langle \phi_\beta(\mathbf{r}-\mathbf{R}_l)\,|\,\phi_\alpha(\mathbf{r})\rangle + \sum_{\mathbf{R}_l} e^{i\mathbf{k}\cdot\mathbf{R}_l}\langle \phi_\beta(\mathbf{r}-\mathbf{R}_l)\,|\,\hat{H}\,|\,\phi_\alpha(\mathbf{r})\rangle - E_{(\mathbf{k})}^{n}\sum_{\mathbf{R}_l} e^{i\mathbf{k}\cdot\mathbf{R}_l}\langle \phi_\beta(\mathbf{r}-\mathbf{R}_l)\,|\,\phi_\alpha(\mathbf{r})\rangle \right| = 0 \ . \tag{2}$$

ε_α is the corresponding Coulomb integral, for which a modified Herman-Skillman[7] (HS) atomic value[4] was used in the present band calculation. The interatomic matrix element was also estimated by Harrison's method.[8] Details of this semiempirical method have been reported in our previous papers.[1,4]

In terms of the LCAO Bloch crystal orbital $\Psi_{\mathbf{k}}^{n}(\mathbf{r})$, the electron CD, $\rho(\mathbf{r})$, is given as

$$\rho(\mathbf{r})=q\sum_{n,\mathbf{k}}^{\mathrm{occ}}|\Psi_{\mathbf{k}}^{n}(\mathbf{r})|^{2}=q\sum_{n,\mathbf{k}}^{\mathrm{occ}}\sum_{\alpha}\sum_{\beta}[C_{\alpha}^{n}(\mathbf{k})]^{*}C_{\beta}^{n}(\mathbf{k})\phi_{\alpha}^{*}\phi_{\beta}\ . \tag{3}$$

The LCAO basis ϕ_α, located at $\mathbf{R}_l$ with the (n,l,m) eigenstate, can be decomposed into a radial part P_{nl}^{α} and an angular part Y_l^m. Consequently, $\rho(\mathbf{r})$ is rewritten as

$$\rho(\mathbf{r})=q\sum_{n,\mathbf{k}}^{\mathrm{occ}}\left[\sum_{\alpha}\sum_{\beta}[C_{\alpha}^{n}(\mathbf{k})]^{*}C_{\beta}(\mathbf{k})P_{n_{\alpha}l_{\alpha}}^{\alpha}(r_{\alpha})P_{n_{\beta}l_{\beta}}^{\beta}(r_{\beta})[Y_{l_{\alpha}}^{m_{\alpha}}(\theta_{\alpha},\varphi_{\alpha})]^{*}Y_{l_{\beta}}^{m_{\beta}}(\theta_{\beta},\varphi_{\beta})\right]\ , \tag{4}$$

where $\mathbf{r}_\alpha=(r_\alpha,\theta_\alpha,\varphi_\alpha)$ is the corresponding positional vector from the $\mathbf{R}_\alpha$ center. In the present $\rho(\mathbf{r})$ calculation, the LCAO coefficients $C_\alpha^n(\mathbf{k})$ determined from Eq. (2) were used. The HS numerical wave functions[7] were also used as approximate radial wave functions.

The atomic geometry of the skeleton of the polysilane model compound is assumed to be *trans*-planar. Alkyl side chains are also assumed to form an all-trans-type geometry. The resulting organopolysilane, —(SiXY)$_n$—, has a symmetry of D_{2h} for $X=Y$ and C_{2h} for $X\neq Y$. The Φ side groups in phenylpolysilane are initially arranged to form a vertical dihedral angle between the skeleton plane and the Φ molecular plane (called here, the initial arrangement). This dihedral angle was then varied to investigate the effect of the rotation of the Φ side group. The bond lengths used here were quoted from Phillips rationalized radii.[9] Here, the Si skeleton is oriented parallel to x axis, and also the skeleton plane is in the xy plane. Thereby, side groups pend toward the z-axis direction.

III. RESULTS

A. Skeleton–side-group interaction at the band edges

Dimethylpolysilane (DMePSi), —(SiMe$_2$)$_n$—, is a typical alkylpolysilane with a methyl (Me) side group. The calculated electronic structure is shown in Fig. 1. One characteristic feature is that both the valence-band top state (HOVB) and the conduction-band bottom state (LUCB) are σ-electronic states delocalized along the Si skeleton; HOVB is the bonding state between the skeleton Si $3p_x$ (along the skeleton axis) AO's with B_{2g} symmetry and LUCB is the antibonding state between the Si 3s AO's with B_{3u} symmetry. The occupied-band state appearing between ≈ -14 and -11 eV is a skeleton pseudo-π band, which is produced by π-π coupling between neighboring Si 3p AO's (standing vertically on the Si skeleton plane). This band state contributes to the bond formation connecting the side groups to the Si skeleton.

According to these results, the requirement for the skeleton–side-group interaction in polysilane can be revised as follows: (i) the magnetic quantum numbers of the corresponding AO's in the side chain need to be equal to that of the Si $3p_x$ AO, and (ii) the mixing eigenstates of the side groups must be in the region of the skeleton σ HOVB state of ≈ -8 to -9 eV.

The HOMO states of benzene (phenyl side group) are doubly degenerate π states of C 2p AO's, whose orbital lobes stand vertically on the molecular plane. Their energy eigenvalue is 9.25 eV, which is comparable to that of the HOVB of polysilane. These cause the σ-π band mixing between the Si-skeleton delocalized σ HOVB state and Φ–side-group localized π HOMO states in phenylpolysilane (Fig. 2). This σ-π band mixing also results in the following complex VB-edge structure, because of the double degeneracy of the Φ π HOMO's (Refs. 10 and 11). Three occupied levels are initially formed. The symmetric Φ π HOMO (corresponding to benzene e_{1g}^{s} π HOMO) is able to mix with the skeleton delocalized σ HOVB state. This results in the formation of two σ states (D_1 and D_2). The periodic arrangement

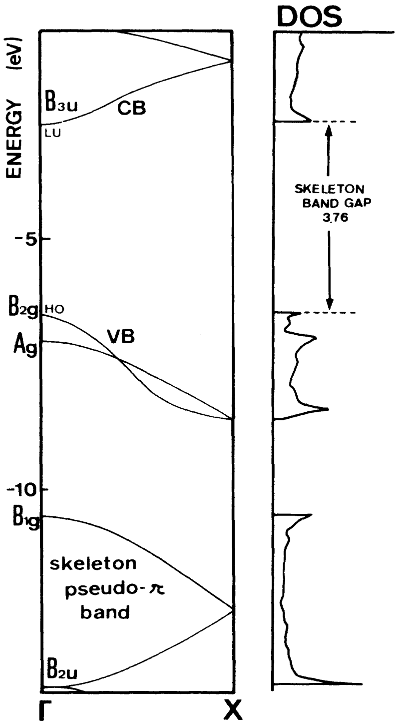


FIG. 1. Calculated energy band structure near band edges for DMePSi. Density of states (DOS) is also given on right.

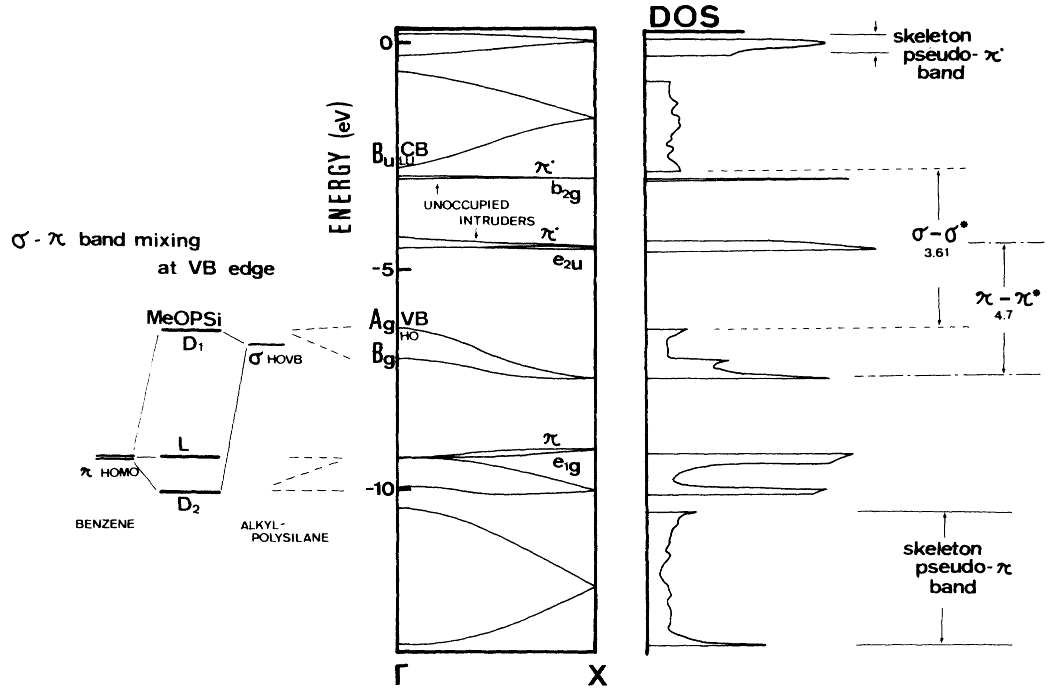


FIG. 2. Calculated energy band structure near band edges for MeΦPSi. Schematic σ-π band mixing is also given on left.

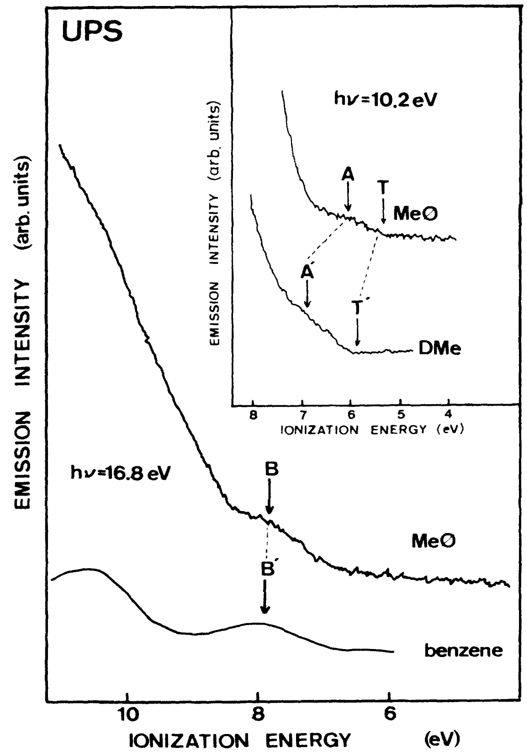


FIG. 3. UPS of MeΦPSi excited by Ne I (16.8 eV) and H Lyman-α (10.2 eV) emission. UPS of DMePSi and solid benzene are also given.

of the SiMeΦ segment causes a k dispersion in the E-k relation, and electrons occupying these two states are delocalized along the Si skeleton. The other π HOMO (benzene e_{1g}^{a} π HOMO), however, cancels this σ-π mixing effect owing to its symmetry. The resulting state (L) remains strongly localized in the individual Φ side groups, almost as if no σ-π band mixing had occurred at all. The localization of the L state is strengthened when

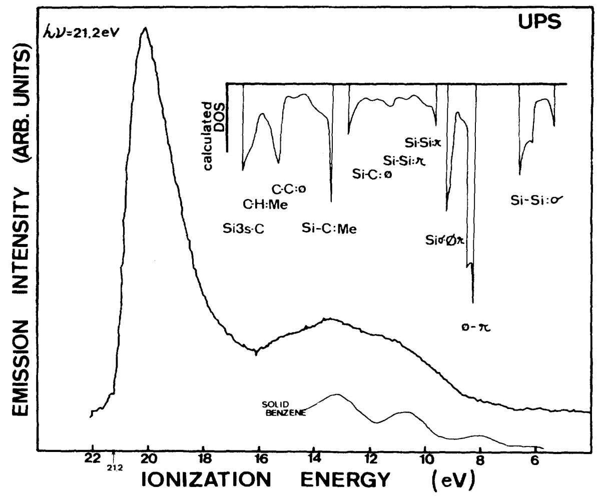


FIG. 4. UPS of MeΦPSi excited by He I (22.1 eV) emission. Calculated DOS are also given.

a longer polymer chain is formed, since the augmentation of the σ HOVB state delocalization enhances the effect of the σ-π band-mixing cancellation.[10] Similar formation of two delocalized and one localized bands has also been observed in other phenyl-containing polymers,[11] but with an important difference that the benzene rings in them are in the principal chain, playing an essential role in electron delocalization.

The skeleton–side-group interaction at the CB edge will be examined next. The LUCB state of polysilane is a σ^*-antibonding state between Si 3*s* AO's. The first three unoccupied states of Φ side groups are π^* states, whose energy positions are located within the band gap of polysilane, and their orbital lobes also stand vertically on the phenyl plane. Thus the orbital orthogonality inhibits the mixing between Si-skeleton-delocalized σ^* state and Φ–side-group localized π^* state at the CB edge. The resulting LUCB state retains the similar energy structure to that of alkylpolysilane (DMePSi). The unoccupied π^* states originating from the Φ side group independently intrude into the skeleton band gap without band mixing.

B. UPS measurements of MeΦPSi

Based on a UPS measurement, we confirmed our theoretical predictions for the characteristic σ-π band mixing at the VB edge of phenylpolysilane. Since the sample preparation and characterization for DMePSi have been reported elsewhere,[12] the present paper reports those for MeΦPSi. MeΦPSi used in the experiment was prepared via a reaction of metyhlphenyldichlorosilane with sodium metal in toluene under an Ar-gas atmosphere,

$$n(\mathrm{Me\Phi SiCl_2})+2n\,\mathrm{Na}\rightarrow(\mathrm{SiMe\Phi})_n+2n(\mathrm{NaCl})\ . \quad (5)$$

Synthesized polymers were purified by three reprecipitations using a benzene-methanole system and dried in a vacuum. MeΦPSi exhibited a single broaden molecular weight distribution with $M_n = 1.6\times10^4$ ($M_w/M_n = 4.5$), where M_n and M_w are the number and weight average molecular weight, respectively. On the contrary, the corresponding molecular weight distribution could not be measured for DMePSi, because this polymer does not have any organic solvent at room temperature.[13] Although x-ray diffraction measurements were also carried out for the cast films of the polymers, synthesized MeΦPSi seems to be in the noncrystalline state, because sharp diffraction peaks were not observed. Characterization of the purified polymers was carried out by the conventional techniques of infrared (ir), ^{1}H, ^{13}C, and ^{29}Si NMR, and also uv (Ref. 4) absorption spectroscopy. According to the ir spectra, the siloxane structure could not be found, and NMR measurements confirmed the chain structure of the synthesized polymers.

Since organopolysilanes are hardly oxidized, as shown by Loubriel and Zeigler[5] using Auger spectroscopy, samples spin coated onto a copper substrate from benzene solution were immediately transferred to the UPS chamber and also pumped down to vacuum in the present experiment. Photoelectron-spectroscopic measurements were carried out by using the retarding-field UPS technique[14] at room temperature under a vacuum of 10^{-4} Pa. The light source was a dc discharge lamp capable of He I (21.2 eV), Ne I (16.8 eV), and H Lyman-α (10.2 eV) emission. This light source was also coupled to a monochromator (Minuteman 302VM) so as to have corresponding single-photon-energy spectrum. Sample charging could be avoided by adjusting the sample thickness and using weak uv light. The absence of sample charging is verified by the sharpness of the cutoff of the spectra at the corresponding excitation energies (e.g., left-hand cutoff of Fig. 4). These weak uv lights also did not change anything in UPS signals before and after the irradiations, and during the irradiations. This fact means that the excitation uv light does not degrade organopolysilane samples. Thus UPS of reasonably good quality could be measured.

Theoretically, two results were presumed to occur due to the σ-π band mixing in MeΦPSi: first, the localized state (L) on the individual Φ side chains retains an energy eigenvalue equal to that of isolated benzene; second, the HOVB state of MeΦPSi rises to a higher-energy state than that of alkylpolysilane. What this means is that MeΦPSi is predicted to have a lower first ionization potential value.

Figure 3 shows UPS of MeΦPSi by Ne I (16.8 eV) and H Lyman α (10.2 eV) emission. UPS for solid benzene and DMePSi (Ref. 12) are also shown for comparison. A peak at 8 eV is found in the Ne I spectrum of MeΦPSi. This peak originates from the excitation of electrons localized in the individual Φ side groups, since the ultraviolet photoelectron spectrum of solid benzene shows a peak due to the π HOMO's at the same energy position. The HOVB part of MeΦPSi is very weak and may be due to the incompletely clear sample surface. Fortunately, this part can be observed clearly at lower $h\nu$ (10.2 eV). The UPS at this energy shows the HOVB energy shift due to σ-π band mixing. The HOVB state of MeΦPSi (6.1 eV) is raised by about 0.7 eV over that of DMePSi (6.9 eV) which has no π electrons. The threshold energy of ionization also shows a corresponding shift from 5.9 eV (T') to 5.3 eV (T).

The agreement of the peaks at 8 eV in the two ultraviolet photoelectron spectra supports our theoretical conclusion that the asymmetric MO state of the doubly degenerate π HOMO's does not mix with the σ states in the principal chain, and that it remains strongly localized in the individual Φ groups almost as if it is an isolated benzene ring. The observed HOVB shift in MeΦPSi from DMePSi also confirmed our theoretical result for the σ-π mixing. The full UPS excited by He I (22.2 eV) emission can be qualitatively assigned as a result of comparison with the calculated density of states (Fig. 4).

We also note the absence of such a large decrease of observed ionization energy in the case of polystyrene ($\mathrm{CH_2}$-$\mathrm{CH\Phi}$), which is the carbon analogue of MeΦPSi, whose ionization threshold (6.95 eV) (Ref. 15) is almost the same as that of solid benzene (7.1 eV). This should be the large difference of the HOMO and/or HOVB energies between benzene and polyethylene.

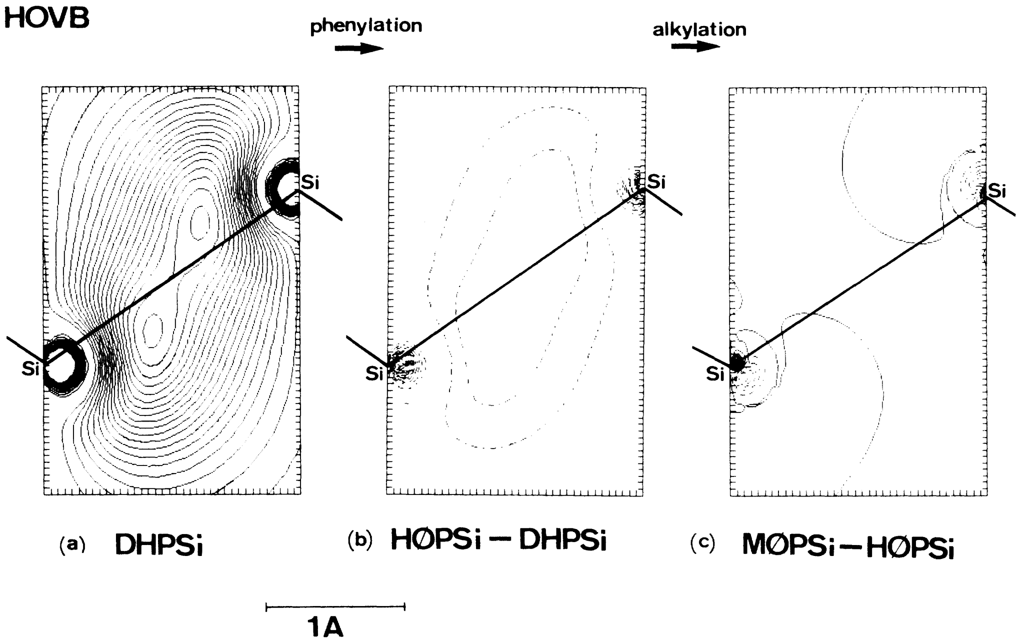


FIG. 5. Calculated CD distribution map of HOVB state on the Si-skeleton plane for DHPSi (a). Difference CD distribution map between DHPSi and HΦPSi (b), and the same between MeΦPSi and HΦPSi (c). In difference CD maps, regions circled by solid lines correspond to the electron-inflowing areas. Those circled by dashed lines correspond to electron-dissipating areas.

C. Phenylation and alkylation in polysilane

Pendants of polysilane can be substituted for several kinds of organo-substituents. Here, it would be opportune to take a theoretical look at the influence of phenylation or alkylation on the band-edge electronic structure. Dihydropolysilane (DHPSi) is chosen as a parent polysilane, since both phenylpolysilane and alkylpolysilane can be derived from this parent. Phenylation or alkylation is here simulated by substituting H atoms of the parent by Φ and Me groups, respectively.

Figure 5(a) shows a CD distribution map of the HOVB state on the Si-skeleton plane in the DHPSi unit cell. The $3p$-like AO character is found at each Si atomic site. The σ bonding between these skeleton Si $3p$ AO's causes the higher CD region appearing at the

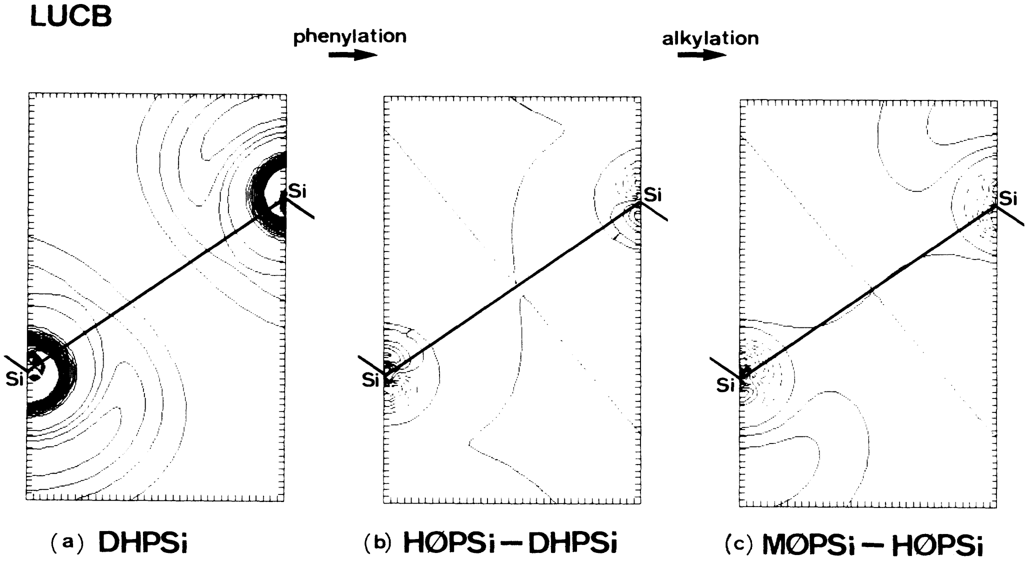


FIG. 6. Calculated CD distribution map of the LUCB state on the Si-skeleton plane for DHPSi (a). Difference CD distribution map between DHPSi and HΦPSi (b), and the same between HΦPSi and MeΦPSi (c). Meaning of solid and dashed lines in difference CD maps is the same as in Fig. 5.

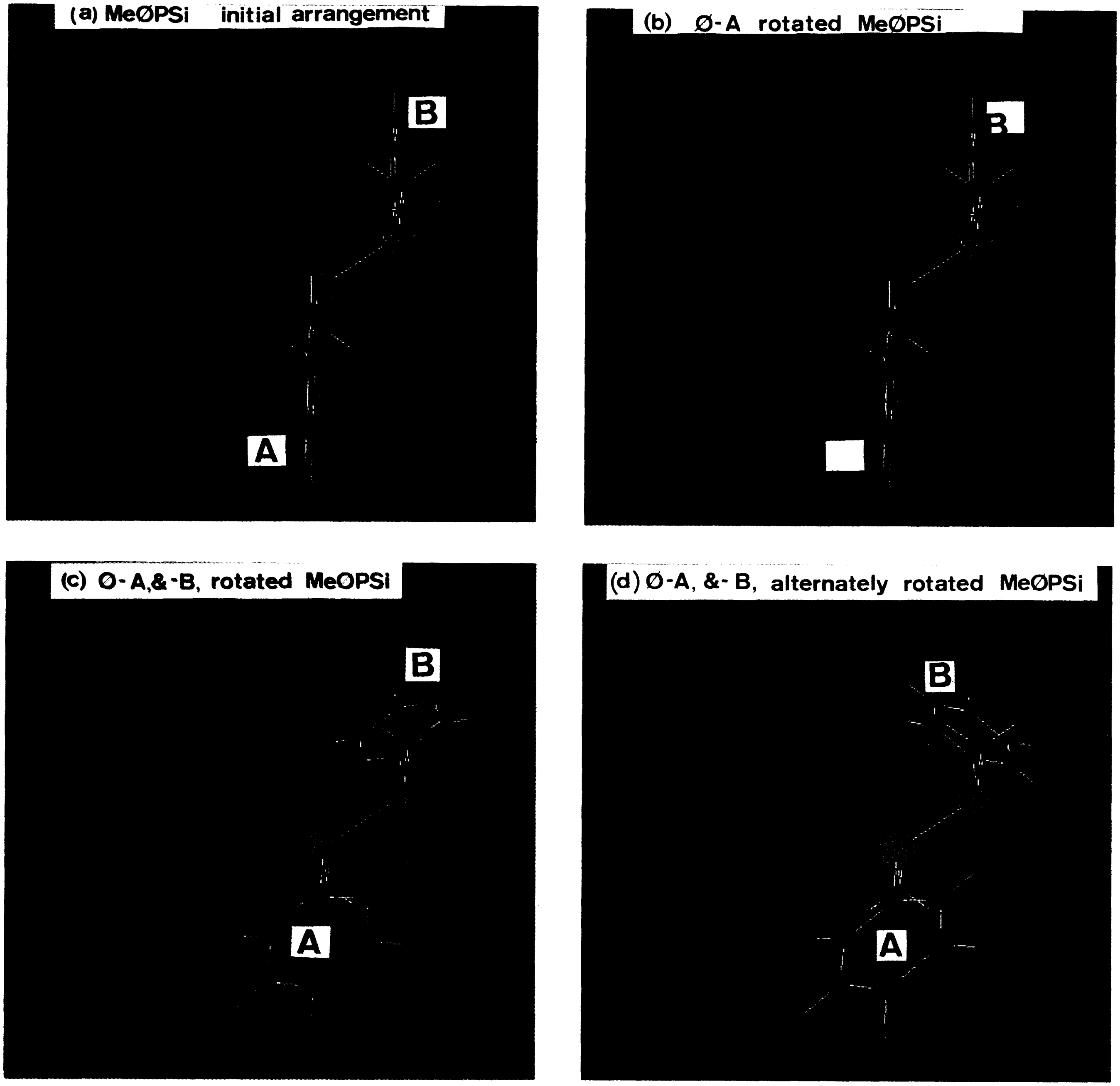


FIG. 7. Illustration of MeΦPSi unit cell with rotated Φ side groups: (a) initial Φ-group arrangement; both phenyl planes in the unit cell are parallel to the *yz* plane, (b) one of the Φ groups (*A*) in the unit cell is rotated about its Si—C bond axis counterclockwise by 60° from the initial arrangement, while the other Φ group (*B*) remains in its initial arrangement, (c) Φ group (*B*) is also rotated about its Si—C bond axis clockwise by 60° from the initial arrangement, (d) Φ group (*B*) is rotated here counterclockwise by 60° from the initial arrangement.

center of the Si skeleton bond. Since the Si $3p$ AO has one nodal character, the zero-CD region is found 0.4 Å away from the Si atomic site.

Substituting one of two H atoms in the DHPSi segment for the Φ group produces HΦPSi (phenylation). The σ-π interaction mixes the π HOMO in the Φ side group with the σ HOVB state. As a result, the contribution from the skeleton Si $3p_x$ AO is reduced, and the CD value is lowered by 31% in the central region of the Si skeleton bond [Fig. 5(b)]. This means that the Φ side group plays a role as an electron acceptor for the delocalized σ HOVB electrons of polysilane and that the phenylation dissipates delocalized σ electrons towards the Φ side groups.

Alkylation can be simulated by substituting the remaining H atoms in HΦPSi for the Me group. The CD value is increased about 29% owing to this methylation at the bond center [Fig. 5(c)]. This CD increase is caused by the electron inflow from Me side chains due to the electron donation of the Me group.

The σ^*-antibonding character of the skeleton Si 3s orbitals results in the formation of a zero CD region in the center of the skeleton bond [Fig. 6(a)]. Two nodal CD regions appearing near Si atom sites are caused by the corresponding nodal planes of the Si 3s AO character. The change in the CD distribution for the LUCB state due to phenylation is not large along the skeleton Si bond [Fig. 6(b)]. The reason is that no σ^*-π^* band mixing occurs at the CB edge. Therefore, the influence of the Φ-group electron acceptation is also weakened compared to that in the HOVB state. The influence of Me-group electron donation is remarkable [Fig. 6(c)]. This is caused by the enhanced Me-group electron-donation mechanism in the LUCB state.

D. Rotation of the Φ side group

Because the skeleton–side-group interaction at the band-edge states of phenylpolysilane is caused by the σ-π (VB edge) or σ^*-π^* (CB edge) band mixing, it is thought to be closely connected to the rotation of the Φ side group. In the preceding section a vertical dihedral angle between the Si skeleton plane and Φ molecular plane was assumed to exist (initial arrangement). We have theoretically investigated the influence of the Φ group rotation on the band-edge electronic structures by rotating a Φ side chain within ±60° from its initial arrangement (Fig. 7).

The initial Φ side-chain arrangement produced the most localized D_1 band state and also the largest energy shift for the HOVB state, i.e., the lowest first ionization potential value (Fig. 8). This is because the Φ side-chain π HOMO's effectively mix with the skeleton-delocalized σ-band state. On rotating Φ side groups, the weakened σ-π band mixing reduces the effective electron-accepting capability of the Φ group. Dissipated electrons are then carried back from the Φ groups towards the skeleton. The resulting CD value of the HOVB state with the rotated Φ side groups [Fig. 7(d)] is augmented by about 7% in the central region of the skeleton bond, relative to that for the initial arrangement [(ii) of Fig. 9]. Thus thermal rotation of the Φ side group will result in an increase of the D_1 band dispersion and delocalization along the skeleton. This type of DOS fluctuation at HOVB due to the thermal rotation of the Ph group is one of the candidates that cause the UPS peaks to broaden. By lowering temperature, the UPS peaks might become slightly sharp owing to the freezing of Φ–side-group rotation (Fig. 4).

On the other hand, the D_2 band state is most delocalized in the initial arrangement. This state becomes localized as Φ side groups rotate. This is because the

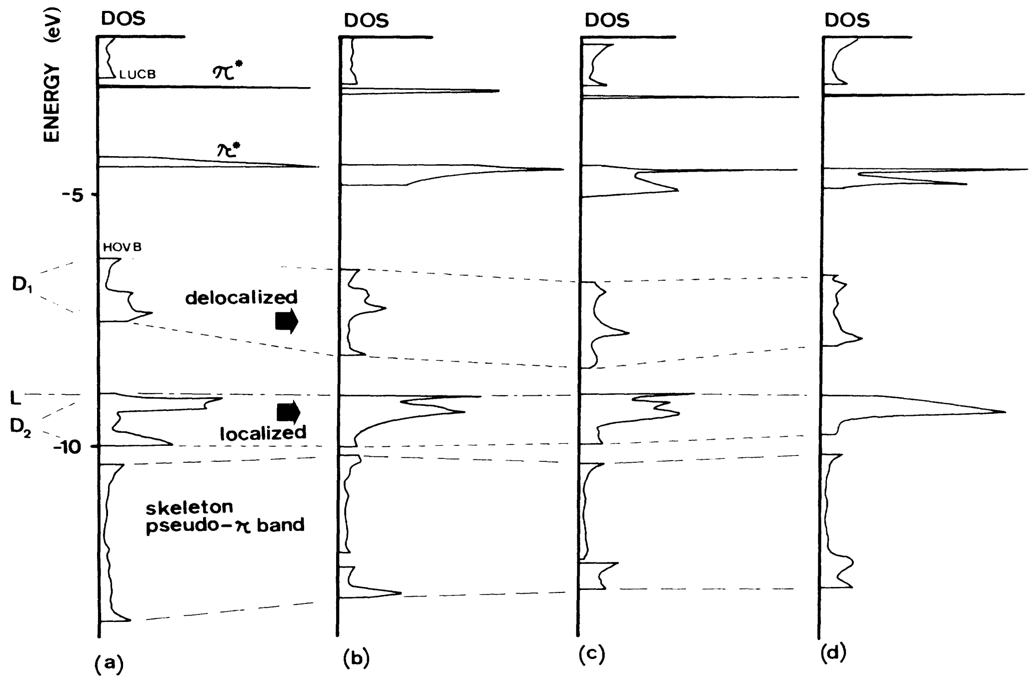
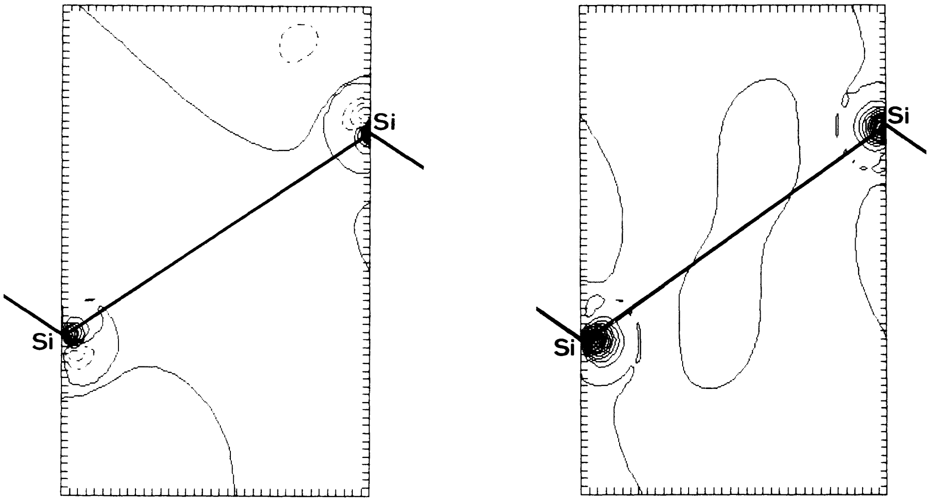


FIG. 8. Change in DOS for MeΦPSi with rotating Φ side groups. (a)–(d) correspond to Φ–side-group arrangements illustrated in Fig. 7.



(i) (ii)

FIG. 9. Change in CD distribution along the Si skeleton with rotating Φ side groups: (i) difference CD distribution between arrangement in Fig. 7(b) and initial arrangement; (ii) that between arrangement in Fig. 7(d) and initial arrangement.

weakened σ-π band mixing reduces the contribution from the delocalized electrons along the Si skeleton. The resulting localized states then play the role of intruders into the polysilane VB state, as if no σ-π band mixing occurred. Weak dispersion appearing in those localized states is caused by the interaction between periodically arranged Φ side groups rather than by the weak σ-π band mixing between skeleton and side groups. The Φ side-chain rotation also reduces the structural symmetry (inversion symmetry), leading to the band splitting at point X (Fig. 10).

The corresponding feature of the σ^*-π^* band mixing at the CB edge is in contrast to that of the σ-π band mixing at the VB edge; the mixing tends to increase as the Φ groups rotate. This is due to the Φ side groups being tetrahedrally connected to the skeleton Si atoms. Rotation of these Φ side groups introduces an inclination of the Φ molecular plane relative to the xz plane. This inclination generates the skeleton–side-group interaction between the Si-skeleton delocalized σ^* state and Φ–side-group localized π^* states (b_{2g}). However, this interaction is weaker than that due to σ-π band mixing. The resulting skeleton σ^*-CB edge is pulled down only slightly.

IV. CONCLUSION

It was seen that organopolysilanes having Φ side groups show the characteristic skeleton–side-group interaction. The σ-π interaction at the VB edge causes not only the delocalized σ states along the Si skeleton, but also the localized π states in the individual Φ side groups. The σ^*-π^* interaction at the CB edge is inhibited owing to the orbital symmetry.

The degree of electron localization along the skeleton was found to be tunable by rotating Φ side groups. The σ-π mixing becomes weak with rotation, while the σ^*-π^* mixing would be enhanced.

The phenyl side group acts as an electron acceptor for the delocalized electrons along the Si skeleton. In contrast, the alkyl side-groups act as an electron donor.

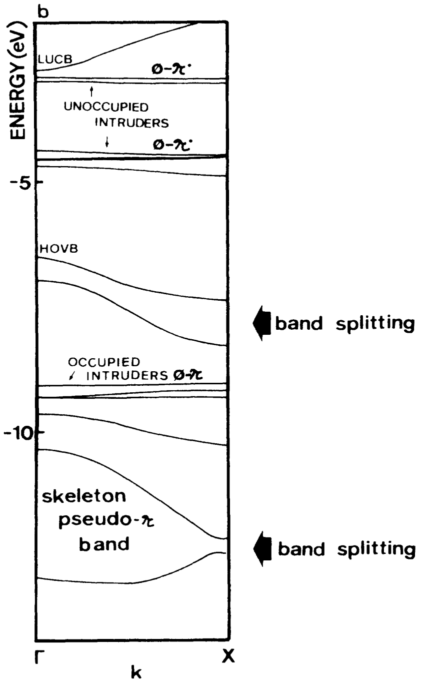


FIG. 10. Band structure of MeΦPSi with arrangement in Fig. 7(b).

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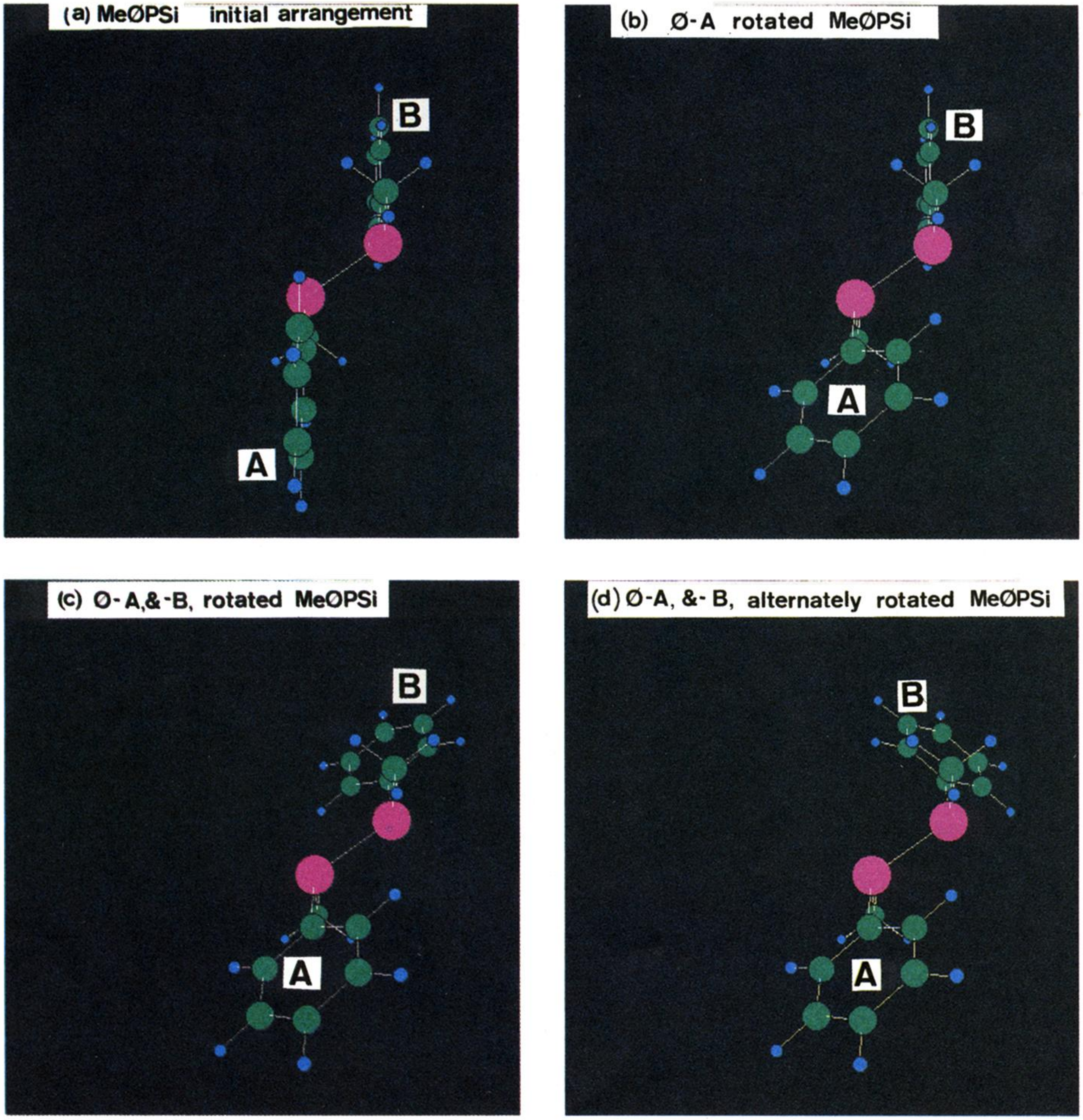

FIG. 7. Illustration of MeΦPSi unit cell with rotated Φ side groups: (a) initial Φ-group arrangement; both phenyl planes in the unit cell are parallel to the *yz* plane, (b) one of the Φ groups (*A*) in the unit cell is rotated about its Si—C bond axis counterclockwise by 60° from the initial arrangement, while the other Φ group (*B*) remains in its initial arrangement, (c) Φ group (*B*) is also rotated about its Si—C bond axis clockwise by 60° from the initial arrangement, (d) Φ group (*B*) is rotated here counterclockwise by 60° from the initial arrangement.