

# Resistivity Mechanisms in Phthalocyanine-Based Linear-Chain and Polymeric Conductors: Variation of Bandwidth with Geometry

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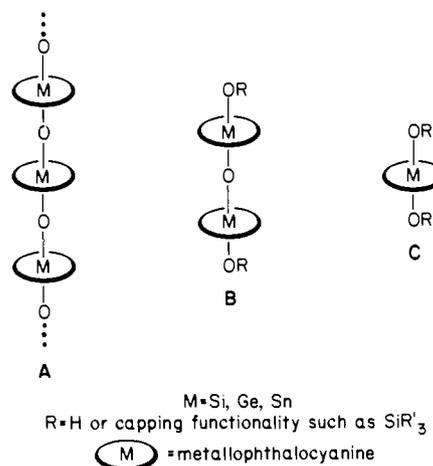
Contribution from the Department of Chemistry and the Materials Research Center, Northwestern University, Evanston, Illinois 60201. Received December 26, 1984

**Abstract:** The Wolfsberg-Helmholtz correlation between overlap and exchange integrals has been employed along with a tight-binding band scheme to study the effects of various geometric distortions on the calculated bandwidths of the phthalocyanine-based polymeric conductor  $[\text{Si}(\text{Pc})\text{O}]_n$  (Pc = phthalocyaninato). Importantly, the Wolfsberg-Helmholtz parameterization constant has been calculated for the overlapping, cofacial  $\pi$  systems in a dimeric fragment of the polymer by using coulomb and exchange integrals and molecular wave functions derived from an all-electron ab initio DVM- $X\alpha$  calculation on the monomeric phthalocyanine subunit. The results indicate that bandwidths calculated by using a simple Wolfsberg-Helmholtz type correlation with properly calculated parameters are in remarkably good agreement with those calculated from DVM- $X\alpha$ . Consequently, the determination of phonon- and libron-induced modulations of polymeric bandwidths in such conductors requires high-level electronic structure calculations only for the monomeric subunits. The phthalocyanine motions parallel to the Si-O-Si backbone and the rotations about this backbone appear to dominate the resistivity, since their electron/vibration coupling constants are large.

A large number of quasi-one-dimensional electronic conductors have been prepared and characterized within the past two decades. These conductive stacks or polymers may be classified in several ways, but one dominant class consists of those materials composed of planar molecules stacked upon one another like poker chips in straight or canted arrays. Representative species in this class include TTF salts, TCNQ salts, and metallophthalocyanine (M-(Pc)) stacks and polymers.<sup>1</sup> Although materials in this class often exhibit unusual transport properties, due to their reduced dimensionality (for example, Peierls' transitions and rather special temperature dependence of the conductivity), they may still, in general, be understood fairly well with simple tight-binding band theory<sup>2a</sup> as exemplified by the extended-Hückel calculations of Grant on TMTSF stacks.<sup>2b,c</sup> Since, however, the bands are quite narrow (from ca. 0.1 to ca. 1.0 eV), these species should show substantial resistivity arising from vibronic coupling. Such couplings limit the conductivity along the chain of these one-dimensional metals, just as they are responsible for the resistivity in good metals.

The tight-binding band and the role of vibronic coupling in providing the resistivity make single-crystal linear-chain conductors similar to ordinary good metals. Two major differences, however, are first that the local electronic functions that participate in the band are atomic s functions in the case of a metal like Na, but are delocalized molecular  $\pi$  orbitals in a TCNQ or phthalocyanine conductor, and second that the local site can undergo, in addition to the usual translational motions that result in phonons in any crystal lattice, rotations and librations and intramolecular vibrations of the planar molecule itself. These motions will cause modulation of the local site energy (for the intramolecular vibrations) or of the effective transfer integral determining the bandwidth (for translations, librations, and vibrations of the rigid planar system about the equilibrium lattice position) and will therefore lead to scattering and contribute to the resistivity along the chain. Moreover, for proximate delocalized  $\pi$  systems, the overlap or transfer integrals are especially sensitive to rotations or librations, and a number of experimental and theoretical efforts have been made to characterize carefully just which electron/vibration and/or electron/libration couplings in fact dominate in determining the resistivity for these species.<sup>3</sup>

Structure-enforced polymers composed of cofacially arrayed group 14<sup>13</sup> phthalocyanine molecules (A) are particularly attractive low-dimensional materials for a variety of reasons.<sup>4</sup> They are easily prepared, relatively inexpensive, air and water stable,



thermally stable to well over 400 °C, chemically rather inert, and highly conductive when doped (partially oxidized or reduced).<sup>4</sup>

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They can be doped with a wide variety of electronically and structurally diverse reagents at various stoichiometries with essentially complete retention of the stacking architecture. Moreover, the phthalocyanine ring may be easily functionalized, affording a wide variety of cofacial polymers.<sup>5</sup> By comparison of experimental results for such systems, qualitative and quantitative ideas about conduction mechanisms and magnitudes as well as how these properties vary with interplanar spacing and off-axis counterion may be derived. Precisely such a series of investigations is being carried out for these polymers by a wide variety of techniques (EPR, dc conductivity, optical reflectivity, solid-state NMR, resonance Raman spectroscopy, crystallography, magnetic susceptibility, thermopower and Hall effect measurements, etc.). The general picture that is emerging is an increase in tight-binding bandwidth from ca. 0.48 to 0.60 to 0.99 eV as the interplanar spacing is reduced from 3.48 (M = Ge), to 3.30 (M = Si), to 3.24 Å (M = Ni), respectively. Such a structural contraction leads to a significant, monotonic increase in room-temperature electrical conductivity and a temperature dependence of conductivity which is increasingly "metal-like" ( $d\sigma/dT < 0$ ) in the macrocycle stacking direction<sup>4a,c</sup> (of course, interparticle contact resistance and crystallite orientational isotropy impart thermally activated transport character to polycrystalline samples<sup>4a</sup>).

In spite of the wealth of experimental information that is becoming available, little has been done theoretically to investigate the mechanism of resistivity in these linear-chain conductors. Earlier extended-Hückel studies<sup>6a,b</sup> probed electronic structure in [Si(Pc)O]<sub>n</sub> models (or related molecular materials); however, vastly truncated phthalocyanine  $\pi$  systems were utilized. A CNDO/crystal orbital [M(Pc)O]<sub>n</sub> study<sup>6c</sup> utilized truncated phthalocyanine molecules and ground-state polymer structures that were inconsistent with experimental data.<sup>4c</sup> The bandwidths obtained were at considerable variance with both experimental and other theoretical results.

In this contribution we describe a simple, computationally efficient method for calculating conduction bandwidth modulations in phthalocyanine cofacial polymers as a function of vibrationally induced geometric distortions. Importantly, our approach has considerable generality as well as computational efficiency and, in principle, could be applied to virtually any stacked electrically conductive system. The information obtained from this technique can then be used to determine phonon and libron contributions to resistivities in molecular metals.

## Methods

We have previously performed high-level all-electron first-principles electronic structure calculations on the HOSi(Pc)OH monomeric subunit (C, R = H)<sup>7,8</sup> using the discrete variational method (DVM)- $X\alpha$  technique of Ellis and co-workers.<sup>9</sup> The calculated ionization potential and electronic spectrum of C at this level were found to be in excellent agreement with experimental measurements. From these calculations, one-electron

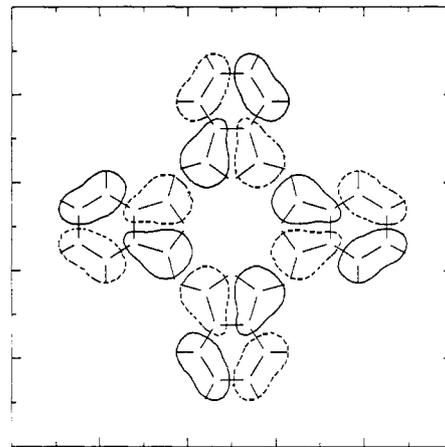


Figure 1. Symmetry and location of the  $a_{1u}$  highest occupied molecular orbital of HOSi(Pc)OH.

Table I. Exponents and Expansion Coefficients for Gaussian Fit to LCAO-DVM Molecular Wave Function for the Symmetry-Nonequivalent Centers in  $a_{1u}$  HOMO of Si(Pc)(OH)<sub>2</sub><sup>a</sup>

parameter	Gaussian		
	1	2	3
$\xi_\alpha$	1.003	0.743	0.166
$C_{1\alpha}$	0.029	0.137	0.156
$C_{2\alpha}$	0.008	0.016	0.025
$C_{3\alpha}^b$	-0.024	-0.072	-0.110
$C_{4\alpha}$	-0.019	-0.049	-0.079

<sup>a</sup> The numbering ( $n$ ) for the nonequivalent carbon centers is as follows:



<sup>b</sup> The change in sign of the coefficients reflects the symmetry of the  $a_{1u}$  HOMO.

eigenvalues ( $\epsilon_i$ ) and molecular wave functions for C have been obtained. Since the DVM- $X\alpha$  method produces numerically defined wave functions, tail regions several angstroms from the nuclear framework are well described. Thus, the DVM- $X\alpha$  method possesses a great advantage over other electronic structure techniques when applied to systems involving long-range electronic interactions such as those occurring in stacked conductors. The absence of an analytical form for the molecular wave functions, however, hinders their subsequent use independent of the DVM- $X\alpha$  program. We therefore expanded the numerical wave function for the highest occupied molecular orbital of HOSi(Pc)OH (C) in a linear combination of Gaussian-type orbitals (eq 1). In eq

$$\psi_{\text{HOMO}} \approx \sum_{\lambda=1}^4 \sum_{\alpha=1}^3 C_{\lambda\alpha} u_\alpha \quad (1)$$

1  $C_{\lambda\alpha}$  is the expansion coefficient of the  $\alpha$ th Gaussian basis function  $u_\alpha = Nze^{-\xi_\alpha r^2}$ , where  $\xi_\alpha$  is the Gaussian exponent and  $N$  is the normalization constant. Since the HOMO is an out-of-plane  $\pi$  orbital and is localized entirely on the four symmetry-nonequivalent types of carbon atoms (Figure 1) of the phthalocyanine ring (designated by  $\lambda$  in eq 1), only  $2p_z$ -type Gaussian functions were used (the  $z$  axis is normal to the ring plane) and were placed only on the carbon centers with three Gaussians per center. The exponents ( $\xi_\alpha$ ) were optimized by a steepest descent method while the expansion coefficients ( $C_{\lambda\alpha}$ ) were fit by least squares. The optimized values are presented in Table I. The Gaussian fit to the numerical wave function is very good. The relative deviation of 300 points, on a line perpendicular to the molecular plane, is only 0.2% between the fit and the DVM orbital.

This analytical solution can now be used to calculate overlap integrals  $S_{12}$  between adjacent phthalocyanine rings in dimer B. A dimer of the form ROSi(Pc)OSi(Pc)OR with R = Si(C-

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**Table II.** Calculated Wolfsberg–Helmholtz Constants for HOSi(Pc)OSi(Pc)OH Dimer<sup>a</sup>

torsion angle, deg	$H_{12}$ , <sup>b</sup> eV	$S_{12}$	$H_{12}$ , <sup>c</sup> eV
0	0.315	0.153	0.315
36.6	0.190	0.093	0.190 <sup>d</sup>
45	0.205	0.101	0.209

<sup>a</sup> $H_{ii}$  value used was  $-4.11$  eV (see ref 7). <sup>b</sup>Calculated by DVM- $X\alpha$ . <sup>c</sup>Calculated by eq 3 with  $\chi_{12} = 0.50$ . <sup>d</sup>The  $\chi_{12}$  value of 0.50 was chosen so that  $H_{12}$  (eq 3) = 0.190 at 36.6°.

$H_3)_2C(CH_3)_3$  has previously been prepared and characterized in this laboratory.<sup>8</sup> Hence, the phthalocyanine cofacial polymers **A** are unique in that both monomer and dimer subunits can be synthesized and studied. By single-crystal X-ray diffraction, the (Pc)Si–O distance in the dimer was found to be 1.615 (2) Å, the Si–O–Si bond angle, 179 (1)°, and the staggering angle of the two Pc rings relative to one another, 36.6°.<sup>8a</sup> Using these geometric parameters (except constraining the Si–O–Si bond to be exactly linear) we have calculated  $S_{12}$  by eq 2. Here  $C_{\lambda\alpha}^{(1)}$  and

$$S_{12} = \langle \psi_1 | \psi_2 \rangle = \sum_{\lambda} \sum_{\lambda'} \sum_{\alpha} \sum_{\alpha'} C_{\lambda\alpha}^{(1)} C_{\lambda'\alpha'}^{(2)} \langle u_{\alpha} | u_{\alpha'} \rangle \quad (2)$$

$C_{\lambda\alpha}^{(2)}$  are the expansion coefficients of the Gaussians on phthalocyanine moieties 1 and 2, respectively, and are fixed by eq 1. The Gaussian overlaps  $\langle u_{\alpha} | u_{\alpha'} \rangle$  have analytical solutions and are easily calculated.<sup>10</sup> The value for  $S_{12}$  at the experimental equilibrium geometry is 0.093. Hence, by using eq 2, we can study the variation of overlap with geometric distortions.

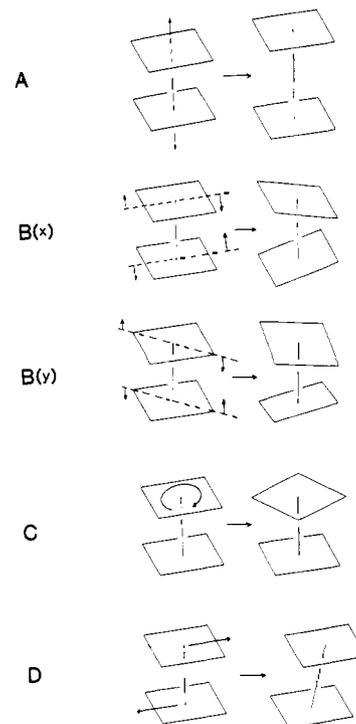
It is well established that overlap integrals,  $S_{ij}$ , may be used to obtain accurate estimates of transfer integrals,  $H_{ij}$ , for adjacent atomic orbitals. This relationship was first proposed by Wolfsberg and Helmholz<sup>11</sup> and is expressed in eq 3, where  $H_{ii}$  and  $H_{jj}$  are

$$H_{ij} \approx \chi_{ij} \frac{H_{ii} + H_{jj}}{2} S_{ij} \quad (3)$$

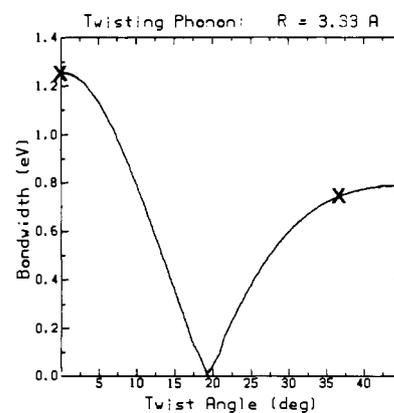
the one-electron energy eigenvalues for atomic orbitals  $i$  and  $j$ , respectively, and  $\chi_{ij}$  is an empirically determined parameter. By substituting the one-electron eigenvalue,  $\epsilon_{\text{HOMO}}$ , of the highest occupied molecular orbital of HOSi(Pc)OH for  $H_{ii}$  and  $H_{jj}$  in eq 3, one obtains a straightforward relationship between  $S_{12}$  (calculated by eq 2) and  $H_{12}$ , which is simply half of the energy splitting of the two highest occupied molecular orbitals in the dimer (our parameter,  $H_{12}$ , is exactly the bandwidth parameter,  $t$ , of tight-binding band theory). For this purpose, the Wolfsberg–Helmholtz constant  $\chi_{12}$  was defined such that  $H_{12}$  (eq 3) equals half the splitting obtained from the previous DVM- $X\alpha$  calculation on the HOSi(Pc)OSi(Pc)OH dimer at the equilibrium geometry (a splitting value in good agreement with gas-phase PES and solid-state optical data).<sup>8a</sup> The value of  $\chi_{12}$  thus determined is 0.50.

## Results

The transfer integrals,  $H_{12}$ , calculated by eq 3 at two other staggering angles, 0 and 45°, compare remarkably well with those determined from the previous DVM- $X\alpha$  study of **B**.<sup>7,8a</sup> These data are presented in Table II. The conduction bandwidth of the infinite polymer **A** is simply 4 times the transfer integral,  $H_{12}$ , of dimer **B**, according to the tight-binding band model.<sup>7</sup> Thus, by using eq 2 and 3, along with the tight-binding band scheme, one may easily investigate bandwidth modulations vs. geometric distortions of the polymer chain. In the case of  $[\text{Si}(\text{Pc})\text{O}]_n$ , the bandwidth should be quite sensitive to the four sorts of motions shown graphically in Figure 2 (accordion-like planar translation along the chain axis (A), tilting motions along (**B**<sub>x</sub>) and between



**Figure 2.** Bandwidth modulating motions of the HOSi(Pc)OSi(Pc)OH dimer: (A) longitudinal stretch; (B) tilt along (x) and between (y) Si–N bond axes; (C) twist; (D) slip.



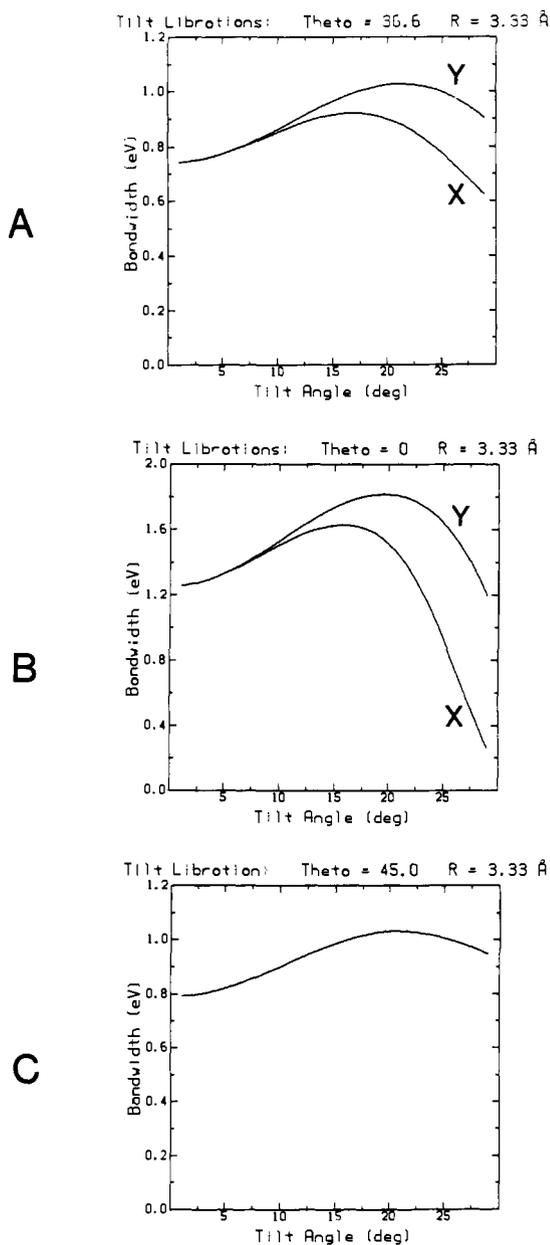
**Figure 3.** Variation of conducting bandwidth with twist angle in cofacially joined phthalocyanine polymers, obtained from eq 3. Points marked  $\times$  indicate those values previously determined by DVM- $X\alpha$  calculations on HOSi(Pc)OSi(Pc)OH.<sup>7,8a</sup>

(B<sub>y</sub>) Si–N bond axes, twist around the chain axis (C), and planar translation perpendicular to the chain axis (D)), which we shall examine. Only the first and last of these correspond to phonons of the type usually encountered in atomic metals.

As indicated by the curve in Figure 3, the bandwidth reaches maxima at the fully eclipsed and fully staggered geometries. A global maximum of 1.25 eV occurs at the eclipsed rotamer. Qualitatively similar results were obtained in an extended-Hückel study.<sup>6a</sup> The curve in Figure 3 also indicates that the bandwidth is quite sensitive to rotational motions of the Pc rings relative to one another at the equilibrium geometry of 36.6°. Moreover, this rotation should be relatively unhindered and therefore occur with a large amplitude. It is interesting to note that the overlap integral changes sign in passing from the eclipsed to staggered forms and, consequently, we predict the band structure of the polymer to vanish at a mutual torsion angle at 19°. This phenomenon has a very interesting consequence. If a cofacial phthalocyanine polymer can be synthesized such that adjacent phthalocyanine rings in the stack are locked (perhaps by steric interactions) at a 19° torsion angle, conductivity can only occur through purely

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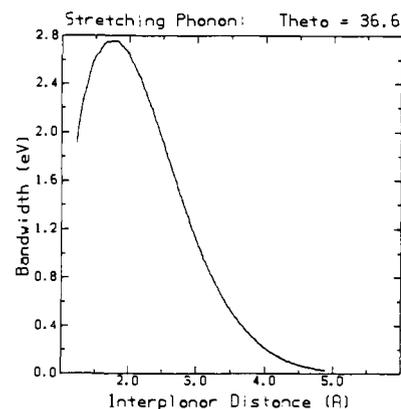


**Figure 4.** Variation of conducting bandwidth with tilt angle along (*x*) and between (*y*) the Si-N bond axes: (A) 36.6° twist angle; (B) fully eclipsed rings; (C) fully staggered rings.

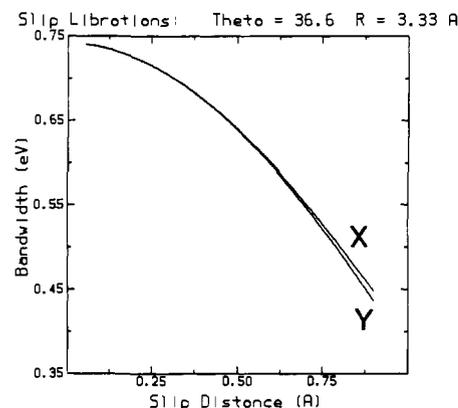
an electron-hopping mechanism. Hence, the material would differ fundamentally from the other stacked phthalocyanine systems in that it would exhibit intrinsically activated conductivity rather than intrinsically metallic.

Figure 4 shows the sensitivity of bandwidth to relative tilt of the two Pc rings with respect to one another. Note that there are two different tilt librations labeled *x* and *y* (see Figure 2B). Although overlap of eclipsed Pc's is quite sensitive to this motion (Figure 4B), still for the experimental twist angle of 36.6°, the variation of *t* with tilt is quite small (Figure 4A); if the twist angle is increased to 45°, the overlap hardly changes with tilt (Figure 4C). Note that at 45° the two tilt librations are degenerate. Since one expects quite substantial increases in nonbonded repulsions as the twist angle increases and the edges of the Pc rings approach one another, the contribution of this tilt motion to the resistivity is expected to be fairly small.

The accordion-like stretching motions along the chain are the longitudinal phonons of the linear-chain conductors. Figure 5 shows the change in bandwidth with this motion. Qualitatively similar results have been obtained in theoretical studies on simpler cofacial  $\pi$  systems.<sup>6a,12</sup> The most substantial changes occur at



**Figure 5.** Variation of conducting bandwidth with interplanar distance in cofacially joined phthalocyanine polymers.



**Figure 6.** Variation of conducting bandwidth with slip distance along (*x*) and between (*y*) Si-N bond axis.

physically unrealistic interplanar spacings between 0.53 and 1.06 Å. For the range of distances near the experimental dimer value of 3.30 Å, the variation in *t* with interplanar separation is somewhat smaller and almost linear (Figure 5). Nevertheless, this variation is still notable, and it might well contribute to the resistivity.

Finally, the variation of the bandwidth with the slip motions, which correspond to transverse phonons or to one Pc unit sliding over another, is shown in Figure 6. The variation is not great, and one expects the energetic cost of distorting the O-Si-O bond from linearity, which would be needed for such a motion to occur, to be relatively large. Thus we suggest that the contribution of these slip motions to the resistivity should be relatively unimportant.

On the basis, then, of our calculations, we infer that the dominant contribution to the resistivity should arise from longitudinal phonons (Figures 2A and 5) and from twisting about the Si-O-Si bond (Figures 2C and 3). The first of these is a phonon mode of the ordinary sort, while the second is called a libron in the language of Weger and collaborators,<sup>3b-d</sup> who have suggested that such motions dominate the resistivity in linear-chain conductors. On the basis of the results presented here, it does appear that these two motions, one phonon and one libron, will dominate the scattering which produces the resistivity, but it is not clear without an actual conductivity calculation which will predominate. As can be seen in Figure 5, the bandwidth is strongly modulated by variation in interplanar spacing, while for twisting motions the matrix element changes its sign as well as magnitude, and the change in total energy is relatively small, since there is little steric

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(13) The group notation is being changed in accord with recent actions by IUPAC and ACS nomenclature committees. A and B notation is being eliminated because of wide confusion. Group I becomes groups 1 and 11, group II becomes groups 2 and 12, group III becomes groups 3 and 13, etc.

(van der Waals) energy change upon twisting (indeed, in the case of the germanium analogue, the relative Pc-Pc staggering angle changes upon partial oxidation, from 0° to 40 (4)°).<sup>4b</sup> The experimental staggering angle in B of 36.6° and in  $\{[\text{Si}(\text{Pc})\text{O}]\text{I}_{1,1}\}_n$  of 39 (3)° comes very near to maximizing the magnitude of the bandwidth; this is important if the stabilizing effect of the partly filled band in the conductive polymer is to be large. More important for present purposes, the high sensitivity of the bandwidth to changes in twist angle implies that this mechanism will effectively scatter the conduction electrons and lead to substantial contributions to the resistivity.

It is clear from the present study that experimental work which either raises the frequency of these two modes or reduces the sensitivity of bandwidth to them will reduce the resistivity. Such work is presently under way in our laboratory.

The success of the Wolfsberg-Helmholtz approximation for calculating  $H_{12}$  and the geometry dependence thereof has interesting consequences. It implies that future electronic structure

studies need calculate only the monomeric subunit of any  $\pi$ -type conductive chain; the expansion of the HOMO in a Gaussian basis as in eq 1 and subsequent calculations using eq 2 and 3 should lead to accurate calculations of exchange integrals and, therefore, of the tight-binding bandwidths. This use of (far simpler) monomer calculations to replace either dimer studies or bandwidth calculations should greatly enhance the value of electronic structure calculations as a screening tool for characterizing and mechanistically understanding linear-chain conductors.

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Registry No.  $[\text{Si}(\text{Pc})\text{O}]_n$ , 39114-20-0;  $\text{HOSi}(\text{Pc})\text{OH}$ , 19333-15-4.

## Stereospecific Formation of Enolates from Reaction of Unsymmetrical Ketenes and Organolithium Reagents

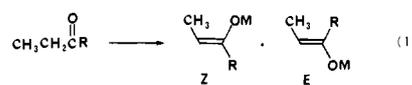
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**Abstract:** Reaction of unsymmetrical ketenes  $\text{RR}'\text{C}=\text{C}=\text{O}$  (**4**, R, R' =  $\text{CMe}_2(\text{CH}_2)_4$ ; **8**, R = Ph, R' = Me; **9**, R = Ph, R' = Et; **10**, R =  $\text{Me}_2\text{Si}$ , R' = Et; **11**, R = *t*-Bu, R' = H) with organolithiums R''Li (R'' = *n*-Bu, Ph, *t*-Bu,  $\text{CH}_2=\text{CH}$ ,  $\text{HC}\equiv\text{C}$ ) followed by silylation with  $\text{Me}_3\text{SiCl}$  gave stereospecific formation of a single silyl enol ether in each case. This result is interpreted in terms of preferential attack by the organolithium reagent in the plane of the ketene from the side opposite the more sterically demanding group. Enolization/silylation of several ketones was carried out and was found to yield additional regio- and stereoisomeric enol ethers besides those formed from the ketenes. Thus the ketene route provides a stereospecific route to silylated enolates that are generally not formed with high selectivity by ketone silylation. Furthermore, a variety of different groups have been incorporated selectively at the different positions of the products. This methodology for stereoselective generation of highly substituted enolate derivatives offers significant advantages over others recently communicated. Hydrolysis of the product (*Z*)- $\text{Me}_3\text{SiC}(\text{Et})=\text{C}(\text{OSiMe}_3)\text{-}n\text{-Bu}$  (**15**) gave  $\text{EtCH}(\text{SiMe}_3)\text{CO-}n\text{-Bu}$  (**29**), so the ketene methodology also is an attractive method for preparation of such  $\alpha$ -silyl ketones.

The generation of enolates and silyl enol ethers of defined *E/Z* stereochemistry at the carbon-carbon double bond is of significant practical importance, as the geometry of these species plays an important role in determining the stereochemistry of the products formed from their aldol reactions under conditions of kinetic control.<sup>1</sup>

There have been a number of recent attempts to control the stereochemistry of enolates, or of silyl enol ethers that may be used to generate enolates. For example, enolization of 3-pentanone (**1**, R = Et) with  $\text{Me}_3\text{SiCH}_2\text{CO}_2\text{Et}$  and *n*- $\text{Bu}_4\text{NF}$  gives the *Z* enol silyl ether with more than 99% selectivity,<sup>2</sup> and the *Z/E* ratio of enolates from this ketone is 30/70, 2/98, and 100/0, using the bases *t*- $\text{Pr}_2\text{NLi}$ , *t*- $\text{Bu}(\textit{octyl})\text{NLi}$ , and  $(\text{Me}_2\text{PhSi})_2\text{NLi}$ , respectively (eq 1).<sup>3,4</sup> When R in **1** is large (Ph, *t*-Bu), several bases



gave the *Z* enolate with 100% selectivity,<sup>3</sup> and in some cases enhanced selectivity for the *E* isomer occurred in the presence of  $\text{Me}_3\text{SiCl}$  to trap the initial enolate formed during the proton abstraction by amide bases.<sup>4b</sup> It was also found possible for particular cases to form *E* and *Z* boron enolates selectively.<sup>5</sup>

There has been considerable discussion<sup>4b,6a,b</sup> as to the origin of the preference for formation of *E* enolates in proton abstraction by bulky lithium dialkylamides in THF, and the model **2** originally proposed by Ireland and co-workers<sup>6b</sup> appears to be the most useful for this purpose.

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