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Bond Rotations and Localization in the Electronic Structure of Polysilanes

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The silicon backbones of polysilanes underlie the many interesting spectroscopic, optical, photochemical, and structural properties exhibited by these polymers.[1,2] Abrupt, temperature-dependent red shifts[3] have been attributed to coil-to-rod transformations and to shorter range conformational changes.[4] Increases in pressure may produce red shifts that are sometimes followed by blue shifts at higher pressures.[5] Characterization of the chromophores and their dependence on conformations is essential for judging the relevance of certain models of coil-to-rod transitions that assume localized excitations.[6] A recent semiempirical calculation[7] on $Si_{20}H_{42}$ indicates that introduction of gauche conformational defects in otherwise all-trans chains concentrates the highest occupied molecular orbital, or HOMO (but not the lowest unoccupied molecular orbital, or LUMO), on the longer of the two trans segments separated by the rotated bond. Lifetime measurements on oligomers with silicon backbones of different lengths[8] and transient absorption experiments[9] suggest that polymer chromophores are between 10 and 15 silicons long. An alternative view is based on band calculations[10] in which gauche conformations are introduced in otherwise all-trans unit cells of several sizes. No localization of one-electron states in trans or gauche regions is reported in these investigations. Localization on the longer all-trans segments of the oligomers[7] is held to be an artifact of the semiempirical method.[10]

To resolve this controversy, ab initio electron propagator calculations are undertaken for $Si_{10}H_{22}$. Determinations of electron binding energies and associated one-electron wavefunctions are performed as a function of dihedral angles in the Si backbone with Gaussian 90[11] and EPT90.[12] Because of their success in calculations on oligomers up to Si_5H_{12},[13] effective core potentials and corresponding double-ζ basis sets for Si[14] and H[15] are used. In extensive studies of various approximations involving basis sets, effective core potentials, and correlation methods, excellent agreement with experiment is obtained.[13]

Geometric parameters optimized for shorter chains with larger basis sets are used; full optimizations produce little variation from these values.[16] Dihedral angles defined by four successive Si's in the all-trans chains are 180°. When a gauche rotational defect is introduced, one of these dihedral angles becomes 60°. The notation X–Y, where X and Y are integers labeling Si atoms, denotes the position of the Si-Si bond where rotation to the gauche conformation has taken place. For example, in the 4–5 gauche conformer, the plane defined by Si atoms 3–5 is rotated 60° with respect to the plane of Si atoms 4–6.

Electron propagator theory[17] produces vertical electron binding energies (ionization energies and electron affinities) and corresponding Feynman–Dyson amplitudes. Propagator electron binding energies contain relaxation and correlation corrections to Koopmans's theorem[18] values, the negatives of canonical orbital energies. To every ionization energy, there corresponds a Feynman–Dyson amplitude (FDA)

$$\int \Psi^*_{N-1}(x_2,x_3,x_4,\ldots,x_N) \times \Psi_N(x_1,x_2,x_3,\ldots,x_N)\, dx_2\, dx_3\, dx_4 \ldots dx_N = \phi^{\mathrm{FDA}}(x_1)$$

where the initial state, Ψ_N, has N electrons. Because it is a function of the space–spin coordinates of a single electron, the FDA is a spin orbital. FDAs are defined similarly for electron affinities. In previous studies,[13] diagonal, second-order self-energies have yielded accurate results for chains up to Si_5H_{12}. The diagonal, self-energy approximation, which is employed in all present calculations, yields an FDA which is equal to a canonical orbital, but with an electron binding energy that includes electron correlation. Finally, a renormalized self-energy approximation which is complete through third order[19] is applied to the all-trans structure and a structure with a gauche defect at the 4–5 bond. The third-order and higher corrections are the same in both structures and are used to shift the electron binding energies for the remaining dihedral angles shown in Figure 1. Calculations of this type with the basis sets described above provide an accurate description of photoelectron spectra[13,20] (agreement within 0.1 eV obtains for short oligomers) and are feasible for longer chains.

Calculations on the all-trans chain produce an ionization energy of 8.22 eV and an electron affinity of −1.45 eV. When a gauche conformational defect is introduced in the central Si-Si bond, the ionization energy increases by 0.28 eV and the electron affinity becomes 0.30 eV more negative. Slightly smaller changes take place when the defect is placed in the 4–5 position: 0.24 and 0.23 eV, respectively. Calculations on the latter rotation at intermediate values of the 4–5 dihedral angle show smooth variation of electron binding energies; there is no abrupt energy change. (See Figure 1.) An energy maximum of the neutral molecule occurs when the dihedral angle is 120° and the barrier is about 0.5 kcal/mol at the Hartree–Fock and second-order perturbation theory levels. There is virtually no difference in the total energy between the all-trans form and the structures with gauche defects.

FDAs for each of the structures can be analyzed in terms of Mulliken charges, which sum to 1 electron when all atomic contributions are considered. Table I shows the differences in these charges for the ionization energy (HOMO) and electron affinity (LUMO) FDAs. (Atoms where a single bond rotation has occurred are denoted by asterisks.) For the all-trans case, the largest contributions come from the central Si atoms. Upon introduction of a gauche defect in the central Si-Si bond, two symmetry-related all-trans segments are created. The most important change is the depletion of charge in Si atoms 4 and 7, the neighbors of the Si atoms where the rotation has taken place. Even this change only amounts to 0.03 electrons for each Si in the ionization energy case. (A similar reduction in the charges of Si atoms next to gauche defects occurs in the highest occupied molecular orbital of the $GTGT_3$ polymer.[10]) For the electron affinity, there is a larger depletion of charge in the same atoms (0.06 electrons) and a small accumulation of charge in atoms 5 and 6 (0.03 electrons).

Asymmetric redistributions take place when a gauche defect, introduced in the 4–5 bond, eliminates all point group symmetry operations. Atomic charges increase in the longer of the two trans segments and decrease in the shorter segment. The changes are largest for atom 3, where losses of 0.06 and 0.10 electrons occur for the ionization

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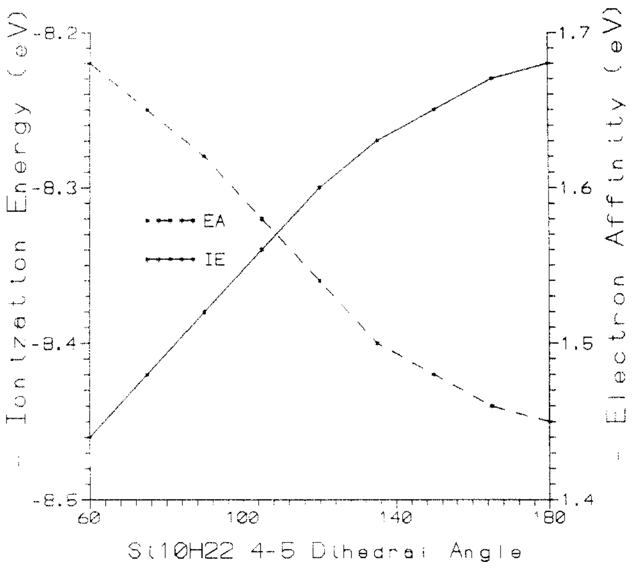

Figure 1. Ionization energy and electron affinity as a function of the 4–5 dihedral angle.

Table I. $Si_{10}H_{22}$ Mulliken Charges

	ionization energy			electron affinity		
Si atom	trans	5–6	4–5	trans	5–6	4–5
1	0.035	0.040	0.019	0.051	0.050	0.020
2	0.069	0.076	0.036	0.073	0.088	0.027
3	0.104	0.102	0.042	0.104	0.109	0.000
4	0.132	0.106	0.114*	0.126	0.064	0.125*
5	0.150	0.158*	0.148*	0.139	0.172*	0.145*
6	0.150	0.158*	0.151	0.139	0.172*	0.139
7	0.132	0.106	0.159	0.126	0.064	0.168
8	0.104	0.102	0.142	0.104	0.109	0.155
9	0.069	0.076	0.102	0.073	0.088	0.108
10	0.035	0.040	0.054	0.051	0.050	0.082

energy and electron affinity FDAs. Atom 7, which lies in the middle of the longer all-trans segment, has the largest contribution to the FDA. When the combined charges of atoms 1–4 are plotted as a function of dihedral angle (Figure 2), one observes that the slope becomes more negative as the gauche conformation is approached. Changes in populations are minor in the vicinity of the all-trans structure.

One can summarize the results as follows. First, gauche defects increase the energy gap between the cation and the anion states. Second, a small deviation from a trans conformation on one bond has no major effect on electron binding energies or on corresponding FDAs. Third, when a gauche defect lies between two all-trans segments of unequal lengths, the FDAs concentrate on the longer segment. Fourth, when a gauche defect creates symmetry-related, all-trans segments, the FDAs remain symmetry-adapted. (Calculations where translational symmetry is imposed on unit cells with various numbers of gauche conformations are likely to produce symmetry-adapted, one-electron states as well.) An extensive study of chains from Si_6H_{14} to $Si_{10}H_{22}$[21] obtains similar results and demonstrates that these conclusions apply to longer oligomers.

In general, polymers exhibit a distribution of dihedral angles; symmetry relationships between all-trans segments separated by a gauche defect are quite unlikely. It is not certain whether localization in an all-trans segment requires the presence of gauche defects or merely a random distribution of dihedral angles about 180°.[22] From this work, there is additional evidence for two propositions. In a polymer, a gauche defect can produce one-electron states that reside chiefly on the longer of the resulting all-trans

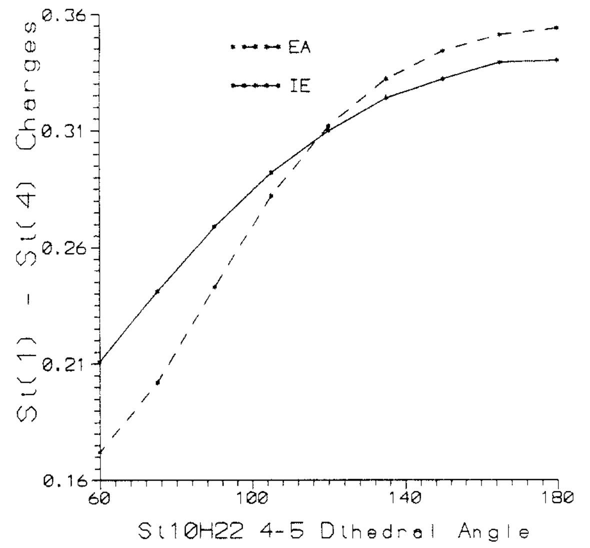

Figure 2. Sum of Mulliken charges for Si atoms 1–4 in ionization energy and electron affinity Feynman–Dyson amplitudes as a function of the 4–5 dihedral angle.

segments. However, a single, small deviation from a trans conformation is not sufficient to produce comparable localizations.

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